

# *A Kinetic Study of the Oxidation of an Alcohol by Dichromate Ion*

## *Introduction to Kinetics*

A general rate expression for the reaction  $A + B + C \rightarrow D + E + F$  would be

$$\frac{\Delta[A]}{\Delta t} = -k[A]^x[B]^y[C]^z \quad (\text{EQ 6.1})$$

read as "The molar concentration of reactant A decreases with time in proportion to the instantaneous molar concentration of A to the  $x^{\text{th}}$  power times B to the  $y^{\text{th}}$  power times C to the  $z^{\text{th}}$  power." The values of  $x$ ,  $y$  and  $z$  are respectively the orders of the reaction in A, B and C. The overall reaction order would be  $x + y + z$ . The letter  $k$  represents the specific rate constant for the reaction.

The reaction conditions may be arranged such that the values of [B] and [C] remain essentially constant over the course of the reaction. For instance, if  $[B]_0 = [C]_0 = 1.000$  and  $[A]_0 = 1 \times 10^{-3}$ , according to stoichiometry of the reaction at  $t = \infty$ ,  $[B] = [C] = 0.999$  and  $[A] = 0$ . Thus, [B] and [C] and therefore  $[B]^y$  and  $[C]^z$  are essentially constant. The rate expression then becomes

$$\frac{\Delta[A]}{\Delta t} = -k[A]^x[B]^y[C]^z = -k_{\text{obs}}[A]^x \quad (\text{EQ 6.2})$$

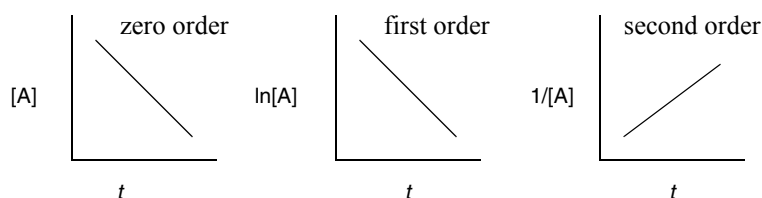
wherein  $k_{\text{obs}}$  (the observed rate constant) is equal to  $k[B]^y[C]^z$ . This is then a pseudo- $x^{\text{th}}$  order reaction, where  $x$  = the reaction order in [A]. i.e. if  $x = 1$  the reaction is pseudo-first order, if  $x = 2$  it is pseudo-second order. As only [A] is changing, only the effect of [A] on the rate is observed.

The value of  $x$ , hence the kinetic order in [A], may be determined by observing the change in the value of [A] as the reaction proceeds. The integrated rate expressions for zero, first and second order reactions are given in Equation 6.3

$$\begin{array}{ll} \text{zero order} & [A] = -kt + [A]_0 \\ \text{first order} & \ln \frac{[A]}{[A]_0} = -kt \quad \text{or} \quad \ln[A] = -kt + \ln[A]_0 \\ \text{second order} & \frac{1}{[A]} = kt + \frac{1}{[A]_0} \end{array} \quad (\text{EQ 6.3})$$

Each of these expressions is seen to be in the form of a linear equation,  $y = mx + b$  where  $x$  is time and  $y$  is some function of  $[A]$ . A linear plot of  $[A]$  vs  $t$  is observed for a zero order dependence of rate upon  $[A]$ . First order reactions yield a linear plot of  $\ln[A]$  vs  $t$  with a slope of  $-k_{\text{obs}}$ . A linear plot of  $1/[A]$  vs  $t$  indicates a second order dependence of rate upon  $[A]$ . Figure 6.1 illustrates these relationships.

FIGURE 6.1



Having now determined the value of  $k_{\text{obs}}$  and the kinetic order of the reaction in component A, the reaction order in B and C and the value of the specific rate constant  $k$  can be evaluated. Maintaining pseudo- $x^{\text{th}}$  order conditions of relatively large concentrations of B and C, the values of  $[B]$  and  $[C]$  are varied. The effect of variation of  $[B]$  and  $[C]$  on the calculated value of  $k_{\text{obs}}$  will indicate the reaction order in B and in C.

Recall that  $k_{\text{obs}} = k[B]^y[C]^z$ . Consider the example where  $[A] = 1 \times 10^{-3}$  and  $[B] = [C] = 1.000$ . What would be the effect of doubling the concentration of B? If the value  $y = 0$ , then  $[B]^y = [B]_0 = 1$  independent of the value of  $[B]$  and the value of  $k_{\text{obs}}$  would be unchanged. If  $y = 1$  then  $k_{\text{obs}}' = k[2B]^1[C] = 2 k_{\text{obs}}$  and the value of  $k_{\text{obs}}$  is observed to double. If  $y = 2$ , then  $k_{\text{obs}}' = k[2B]^2[C] = 4 k_{\text{obs}}$  and the observed rate constant will quadruple. Table 6.1 gives a summary of these data.:

TABLE 6.1

$y$	$[A]_0$	$[B]_0$	$[C]_0$	$k_{\text{obs}}$
	$1 \times 10^{-3}$	1.000	1.000	$x$
0	$1 \times 10^{-3}$	2.000	1.000	$x$
1	$1 \times 10^{-3}$	2.000	1.000	$2x$
2	$1 \times 10^{-3}$	2.000	1.000	$4x$

A similar series of experiments will serve to evaluate  $z$ . With  $x$  determined by graphical analysis along with  $k_{\text{obs}}$ , and  $y$  and  $z$  determined by variation of  $[B]$  and  $[C]$ , the overall specific rate constant  $k$  may be evaluated for each kinetic run by simply substituting the determined values of each variable into Equation 6.4

$$k = \frac{k_{\text{obs}}}{[B]^y[C]^z} \quad (\text{EQ 6.4})$$

The activation energy for a reaction may be determined by application of the Arrhenius equation in the form:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (\text{EQ 6.5})$$

$E_a$  is the activation energy,  $R = 8.314 \text{ J/K}\cdot\text{mol}$  and  $T_2$  and  $T_1$  are the kelvin temperatures for reactions having rate constants  $k_2$  and  $k_1$  respectively. By determining  $k$  or  $k_{\text{obs}}$  for a reaction at different temperatures maintaining constant reactant concentrations, and substituting the proper values into the expression the activation energy is obtained.

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### *Spectrophotometry*

The amount of visible light a sample absorbs in aqueous solution is in direct proportion to the concentration of the solute according to Equation 6.6

$$A = -\log\left(\frac{I}{I_0}\right) = \epsilon lc \quad (\text{EQ 6.6})$$

where  $A$  = absorbance,  $I$  = light transmitted by the solution,  $I_0$  = light incident upon the solution,  $\epsilon$  = the extinction coefficient (or molar absorptivity),  $l$  = the length of the light path in centimeters and  $c$  = the molar concentration of solute. A related term is the percent transmittance, %T, defined in Equation 6.7

$$\%T = 100\left(\frac{I}{I_0}\right) \quad (\text{EQ 6.7})$$

Rearranging Equation 6.7 for absorbance yields Equation 6.8.

$$A = \log\left(\frac{100}{\%T}\right) \quad (\text{EQ 6.8})$$

It is therefore possible to follow quantitatively the rate of a chemical reaction involving a light-absorbing reactant or product by observing the change in the absorbance of the reactant or product with time.

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### *Purpose*

The specific rate constant at room temperature and the activation energy for the oxidation of isopropyl alcohol by dichromate ion in acid solution will be determined by measuring spectrophotometrically the rate of disappearance of dichromate ion in the course of the reaction under controlled conditions.

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### *Background*

Dichromate ion oxidizes isopropyl alcohol in the presence of hydrogen ion in aqueous solution to yield acetone. In the process, the dichromate ion is reduced to chromium(III) ion. The only reactant that absorbs visible light is dichromate ion which shows a maximum absorbance at 444 nm. The only colored product is chromium(III) ion which does not absorb light at this wavelength. It is therefore possible to utilize the absorbance of the solution at 444 nm as a direct measure of the dichromate ion concentration in a kinetic study of the reaction.

The rate expression for the reaction is written in Equation 6.9.

$$-\frac{\Delta[\text{Cr}_2\text{O}_7^{2-}]}{\Delta t} = k[\text{Cr}_2\text{O}_7^{2-}]^a [\text{H}^+]^b [\text{alcohol}]^c \quad (\text{EQ 6.9})$$

Under conditions wherein  $[\text{H}^+]$  and  $[\text{alcohol}] \gg [\text{Cr}_2\text{O}_7^{2-}]$  the reaction may be considered pseudo- $a^{\text{th}}$  order in dichromate ion, and the concentrations of hydrogen ion and alcohol are constant. Under these conditions  $k_{\text{obs}}$  can be expressed as in Equation 6.10.

$$k_{\text{obs}} = k[\text{H}^+]^b [\text{alcohol}]^c \quad (\text{EQ 6.10})$$

### Procedure

1. The "Spectronic 20" spectrophotometer should be turned on (left-front knob) and allowed to warm up while solutions are prepared. Adjust the wavelength dial to 444 nm with the filter setting in the correct position. Follow the instructions on the instrument to calibrate it before your first use. When you are finished calibrating, make sure that you **set the instrument to measure in absorbance**.
2. Label three clean, dry tubes and as precisely as possible measure, from the burets provided, the following quantities of reagents.

TABLE 6.2

	tube 1	tube 2	tube 3
isopropyl alcohol 0.75M	1.00 mL	2.00 mL	1.00 mL
H <sub>2</sub> SO <sub>4</sub> , 3.0 M	5.00 mL	2.50 mL	2.50 mL
DI H <sub>2</sub> O	0.50 mL	2.00 mL	3.00 mL

3. Measure the temperature of the solutions at the beginning and at the end of the kinetic runs. **Use the average temperature in your calculations.**
4. Rapidly (but precisely) pipet 1.00 mL of  $1.81 \times 10^{-2} M$  potassium dichromate solution into each of the three tubes—stopper and invert to mix—begin reading  $A$  in a rotating sequence at 0.5 min intervals (see Table 6.3 on page 33). Be careful to position the tubes in exactly the same way for each reading. After 22 minutes have elapsed, discontinue readings. After one hour has elapsed since the last reading, read the %T for the tube exhibiting the fastest reaction rate. Use this value for your infinity reading.
5. Repeat the procedure (runs 4 & 5) of runs two and three at a temperature of 35°C. Prepare a water bath at 35°C and equilibrate the tubes containing all reagents except dichromate solution. Equilibrate the dichromate solution separately. Between readings keep the tubes in the water bath. Be careful to dry tubes before each reading. Measure the temperature of the solutions before and after the kinetic runs. Use the average temperature in your calculations. Determine infinity readings after one hour.

### Calculations

Make a table of  $A$ ,  $A - A_{\infty}$  and  $\ln(A - A_{\infty})$  for each of the five kinetic runs. Make a plot of  $\ln(A - A_{\infty})$  vs time for each of the five kinetic runs. From the slopes of the plots determine the observed rate constant for the reaction. From the relationship  $k_{\text{obs}} = k[\text{H}^+]^b [\text{alcohol}]^c$  calculate the overall rate constant for each of the first three runs and report these values and the average value. Use the values of

$k_{\text{obs}}$  and the temperatures for paired runs two and four and three and five to determine the activation energy for the reaction. Report the individual and average values for the activation energy.

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*Sample Notebook Page*

**TABLE 6.3 A Readings at 444 nm (Sample Table)**

	run 1		run 2		run 3	
0.75 M alcohol	1.00 ml	M	2.00 mL	M	1.00 mL	M
3.0M H <sub>2</sub> SO <sub>4</sub>	5.00 ml	M	2.50 mL	M	2.50 mL	M
DI H <sub>2</sub> O	0.50 ml	M	2.00 mL	M	3.00 mL	M
$1.8 \times 10^{-2} M \text{Cr}_2\text{O}_7^{2-}$	1.00 ml	M	1.00 mL	M	1.00 mL	M
	<b>t(min)</b>	<b>A</b>	<b>t(min)</b>	<b>A</b>	<b>t(min)</b>	<b>A</b>
	0		0.5		1.0	
	1.5		2.0		2.5	
	3.0		3.5		4.0	
	4.5		5.0		5.5	
	6.0		6.5		7.0	
	7.5		8.0		8.5	
	9.0		9.5		10.0	
	10.5		11.0		11.5	
	12.0		12.5		13.0	
	13.5		14.0		14.5	
	15.0		15.5		16.0	
	16.5		17.0		17.5	
	18.0		18.5		19.0	
	19.5		20.0		20.5	
	21.0		21.5		22.0	
	∞		∞		∞	
initial temperature			final temperature			

TABLE 6.4 Sample Activation Energy Data Table

Run #	T°C	[ROH]	[H <sup>+</sup> ]	[Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> ]	k <sub>obs</sub>	k

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*Post-Laboratory Questions*

1. The formula for isopropyl alcohol is C<sub>3</sub>H<sub>8</sub>O. The product of the oxidation of isopropyl alcohol is C<sub>3</sub>H<sub>6</sub>O. Write a balanced equation for the oxidation of isopropyl alcohol by dichromate ion in acidic solution.
2. If the observed rate constant for the oxidation reaction at 35.0°C is  $6.75 \times 10^{-2} \text{ min}^{-1}$  and at 25.0°C is  $3.25 \times 10^{-2} \text{ min}^{-1}$ , what is the activation energy for the reaction?
3. What is the rate constant for the reaction in Question 2 at 45.0°C?
4. If the initial concentration of dichromate ion in Question 2 at 25.0°C is  $1.50 \times 10^{-4} \text{ M}$ , what will be the concentration of dichromate at 30.0 min?