5.2: Gas Chromatography Analysis of the Hydrodechlorination Reaction of Trichloroethene

Trichloroethene (TCE) is a widely spread environmental contaminant and a member of the class of compounds known as dense non-aqueous phase liquids (DNAPLs). Pd/Al_2O_3 catalyst has shown activity for the hydrodechlorination (HDC) of chlorinated compounds.

To quantify the reaction rate, a 250 mL screw-cap bottle with 77 mL of headspace gas was used as the batch reactor for the studies. TCE (3 μL) is added in 173 mL DI water purged with hydrogen gas for 15 mins, together with 0.2 μL pentane as internal standard. Dynamic headspace analysis using GC has been applied. The experimental condition is concluded in the table below (Table 5.2.1).

Table 5.2.1 The experimental condition in HDC of TCE.

TCE	3 μL
H_2	1.5 ppm
Pentane	0.2 μL
DI water	173 mL
1 wt% Pd/Al_2O_3	50 mg
Temperature	25 °C
Pressure	1 atm
Reaction time	1 h

Reaction Kinetics

First order reaction is assumed in the HDC of TCE, 5.2.1, where K_{means} is defined by 5.2.2, and $C_{cat}$is equal to the concentration of Pd metal within the reactor and k_{cat} is the reaction rate with units of $L/g_{Pd}/min$.

$$-dC_{TCE}/dt \;=\; k_{meas} \times C_{TCE} \tag{5.2.1}$$

$$k_{meas} \;=\; k_{cat} \times C_{cat} \tag{5.2.2}$$

The GC Method

The GC methods used are listed in Table 5.2.3.

Table 5.2.3 GC method for detection of TCE and other related chlorinated compounds.

GC type	Agilent 6890N GC
Column	Supelco 1-2382 40/60 Carboxen-1000 packed column
Detector	FID
Oven temperature	210 °C
Flow rate	35 mL/min
Injection amount	200 μL
Carrier gas	Helium
Detect	5 min

Quantitative Method

Since pentane is introduced as the inert internal standard, the relative concentration of TCE in the system can be expressed as the ratio of area of TCE to pentane in the GC plot, 5.2.3.

$$C_{TCE} \;=\; (peak\ area\ of\ TCE)/(peak\ area\ of\ pentane) \tag{5.2.3}$$

Results and Analysis

The major analytes (referenced as TCE, pentane, and ethane) are very well separated from each other, allowing for quantitative analysis. The peak areas of the peaks associated with these compounds are integrated by the computer automatically, and are listed in (Table 5.2.4) with respect to time.

Table 5.2.2 Peak area of pentane, TCE as a function of reaction time.

Time/min	Peak area of pentane	Peak area of TCE
0	5992.93	13464
5.92	6118.5	11591
11.25	5941.2	8891
16.92	5873.5	7055.6
24.13	5808.6	5247.4
32.65	5805.3	3726.3
43.65	5949.8	2432.8
53.53	5567.5	1492.3
64.72	5725.6	990.2
77.38	5624.3	550
94.13	5432.5	225.7
105	5274.4	176.8

Normalize TCE concentration with respect to peak area of pentane and then to the initial TCE concentration, and then calculate the nature logarithm of this normalized concentration, as shown in Table 5.2.3.

Table 5.2.3 Normalized TCE concentration as a function of reaction time

Time (min)	TCE/pentane	TCE/pentane/$TCE_{initial}$	In(TCE/Pentane/$TCE_{initial}$)
0	2.2466	1.0000	0.0000
5.92	1.8944	0.8432	-0.1705
11.25	1.4965	0.6661	-0.4063
16.92	1.2013	0.5347	-0.6261
24.13	0.9034	0.4021	-0.9110
32.65	0.6419	0.2857	-1.2528
43.65	0.4089	0.1820	-1.7038
53.53	0.2680	0.1193	-2.1261
64.72	0.1729	0.0770	-2.5642
77.38	0.0978	0.0435	-3.1344
94.13	0.0415	0.0185	-3.9904
105	0.0335	0.0149	-4.2050

From a plot normalized TCE concentration against time shows the concentration profile of TCE during reaction (Figure 5.2.1, while the slope of the logarithmic plot provides the reaction rate constant (5.2.1).

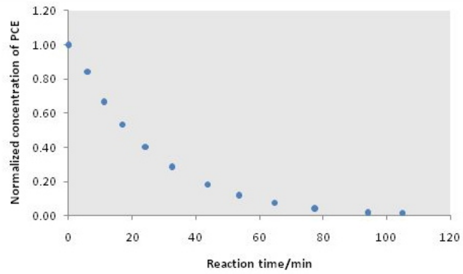

Figure 5.2.1 A plot of the normalized concentration profile of TCE.

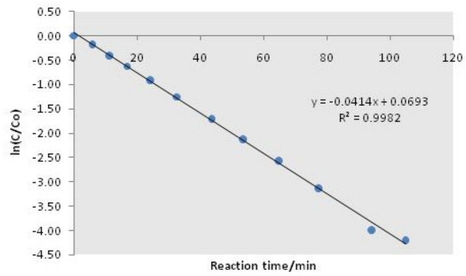

Figure 5.2.2 A plot of $\ln(C_{TCE}/C_0)$ versus time.

From Figure 5.2.1, we can see that the linearity, i.e., the goodness of the assumption of first order reaction, is very much satisfied throughout the reaction. Thus, the reaction kinetic model is validated. Furthermore, the reaction rate constant can be calculated from the slope of the fitted line, i.e., k_{meas} = 0.0414 min^{-1}. From this the k_{cat} can be obtained, ???.

$$\boxed{k_{cat}\ =\ k_{meas}/C_{Pd}\ =\ \frac{0.0414min^{-1}}{(5 \times 10^{-4}\ g/0.173L)}\ =\ 14.32L/g_{Pd}\ min \label{4}}$$