Kinetics of Ethylene Chloride Pyrolysis Using a Pumice Catalyst

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VINYL CHLORIDE is formed by pyrolysis of ethylene chloride:

$$ClCH_2CH_2Cl \xrightarrow{\Delta} CH_2{=}CHCl + HCl$$

Although the reaction is well known and has been studied using a wide variety of catalysts, kinetic studies with heterogeneous catalysts appear to be lacking. The present investigation was carried out at constant pressure using a pumice catalyst and temperatures of 500° to 650° C.

METHODS AND APPARATUS

Equipment. The all-glass apparatus used is shown in Figure 1 and consisted of an ethylene chloride reservoir, preheater, reactor, ethylene chloride recovery vessel, water scrubbers, and a vinyl chloride collector. The reaction tube measured 1.875 cm. inside diameter by 59 cm. long of which a 45 cm. length was kept at a roughly uniform temperature, and all calculations of rate constants were based on this length. The thermocouple well, centered in the reaction tube, measured 0.55 cm. outside diameter. The tube was filled with 6 to 8-mesh pumice stone, which occupied a net space of 53.8 cc. exclusive of free space. The preheater and reactor tube were wound with Nichrome ribbon and insulated with 85% magnesia. The water scrubbers for hydrogen chloride gas were of the submerged column type with a stopcock provided at the base to drain the liquid on completion of a run.

Procedure. Ethylene chloride was fed by gravity from a dispensing buret employing a slight pressure of nitrogen on the liquid to overcome the back pressure. Ethylene chloride passed first to the preheater-vaporizer, then to the reactor. The vapors leaving the reactor were cooled to condense unattacked ethylene chloride which was held under reflux to expel hydrogen chloride. The exit gases from the reflux condenser passed through two water scrubbers to absorb hydrogen chloride, a drying tube, and into the vinyl chloride collector held at −50° C. by dry ice. Noncondensable gases were vented. The aqueous hydrogen chloride collected in the scrubbers was determined quantitatively.

RESULTS

Two specific reaction rate constants, k_1 and k_1', were calculated for comparative purposes and are shown with pertinent data in Table I. The respective k values from the various runs at each temperature agree rather well at low conversions; they show some slight variation with contact time in agreement with the findings of Barton (*1*). The constant, k_1', is the usual one computed from the first order equation,

$$k_1' = \frac{2.303}{t} \log \frac{a}{a - x} \tag{1}$$

where t is the average contact time and a and x have their usual significance. The average contact time, t, which must be computed for dynamic experiments of this type (*1*), was found from the following relation:

$$t = \frac{(LA - TC \text{ well vol.} - \text{catalyst vol.})(3.6)(273)}{22.4m} \left[\frac{1}{T(1 + \alpha/2)}\right] \tag{2}$$

L = length of reaction vessel in cm.
A = cross section area of reaction vessel in sq. cm.
TC = thermocouple
m = input of $C_2H_4Cl_2$ in gram mole per hour
T = temperature of reactor in ° K.
α = conversion or degree of dissociation of $C_2H_4Cl_2$ at the exit end of the tube

Equation 1 holds only for reactions at constant volume. For work done at constant pressure, as in the present study,

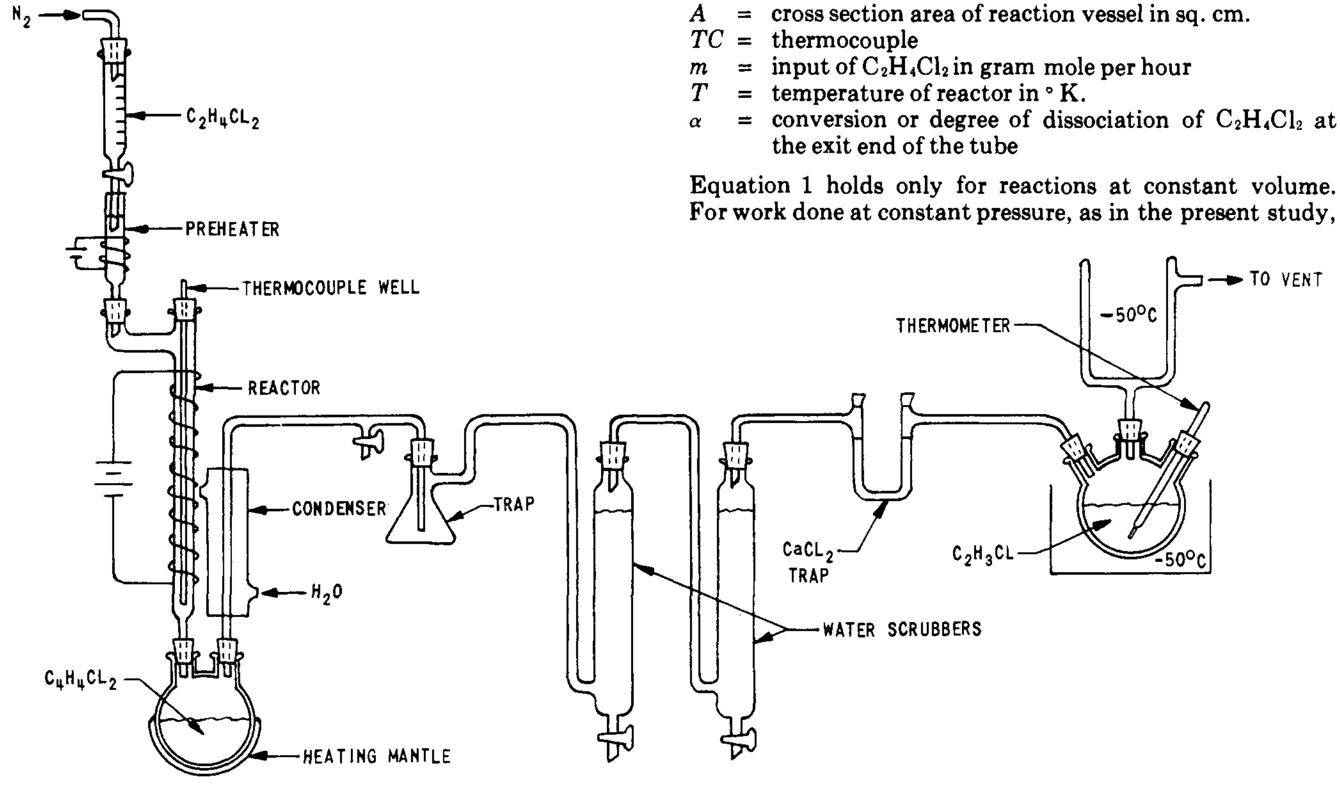

Figure 1. Apparatus for pyrolysis of ethylene chloride

Table I. Effect of Temperature and Contact Time on Specific Reaction Velocity Constant

Temp., °C.	Flow Rate, G. Mole Per Hr.	Conversion	Contact Time, Sec.	k_1' Sec.$^{-1}$	k_1 Sec.$^{-1}$
500	1.117	0.44	2.47	0.234	0.237
500	1.111	0.42	2.51	0.217	0.220
500	0.995	0.49	2.72	0.249	0.255
500	0.95	0.48	2.86	0.229	0.233
500	0.75	0.56	3.52	0.233	0.240
500	0.745	0.63	3.45	0.288	0.300
550	1.92	0.58	1.28	0.675	0.700
550	1.89	0.62	1.28	0.755	0.785
550	1.78	0.68	1.33	0.856	0.900
550	1.20	0.73	1.94	0.674	0.716
550	1.23	0.75	1.88	0.737	0.787
550	0.95	0.81	2.38	0.696	0.754
550	0.97	0.83	2.28	0.775	0.833
550	0.75	0.77	3.06	0.480	0.514
550	0.78	0.83	2.89	0.612	0.667
600	1.98	0.86	1.055	1.82	1.97
600	1.96	0.85	1.07	1.77	1.93
600	1.25	0.91	1.642	1.46	1.63
600	1.24	0.94	1.635	1.72	1.95
600	0.88	0.95	2.31	1.30	1.48
600	0.87	0.96	2.32	1.43	1.64
650	1.871	0.94	1.03	2.73	3.11
650	1.50	0.962	1.272	2.57	2.96
650	1.331	0.98	1.428	2.74	3.22
650	1.122	0.99	1.69	2.73	3.26
650	0.807	0.996	2.34	2.36	2.88

it may be used as a fair approximation for low conversions. The constant k_1 is a more accurate value and is calculated from the first order equation for experiments conducted at constant pressure (2):

$$k_1 \frac{V_r}{V_o} = 2.303\, \nu \log \frac{1}{1-f} - (\nu - 1) f \qquad (3)$$

where

V_r = volume of the reaction zone
V_o = volume of the feed per unit time at the temperature and pressure of the reaction zone.
ν = number of moles of products from 1 mole of reactant
f = fraction of ethylene chloride reacted (= conversion)

For the present case, $\nu = 2$, and Equation 3 reduces to:

$$k_1 = \frac{V_r}{V_o} = 4.606 \log \frac{1}{1-f} - f \qquad (4)$$

Equation 4 may be rearranged to give

$$\frac{V_r}{V_o} = \frac{1}{k_1} \left[-2 \ln (1-f) - f\right] \qquad (5)$$

If time of contact, $\theta = V_r/V_o$ and the concentration factor, $[-2 \ln (1-f) - f] = Z$, then

$$\theta = \frac{1}{k_1} Z \qquad (6)$$

A plot of θ *vs.* Z at various temperatures is given in Figure 2, and the resulting straight lines confirm the reaction as being first order. The average velocity constants at each temperature were computed from the slope of the lines in Figure 2 and a plot of log k_1 *vs.* $1/T$ is shown in Figure 3. From the slope of the line and the intercept, the Arrhenius equation was determined. The energy of activation was found to be 24,500 gram cal. per mole of ethylene chloride and the resulting equation is

$$k_1 = 2.19 \times 10^6 e^{\frac{-24500}{1.987T}} \qquad (7)$$

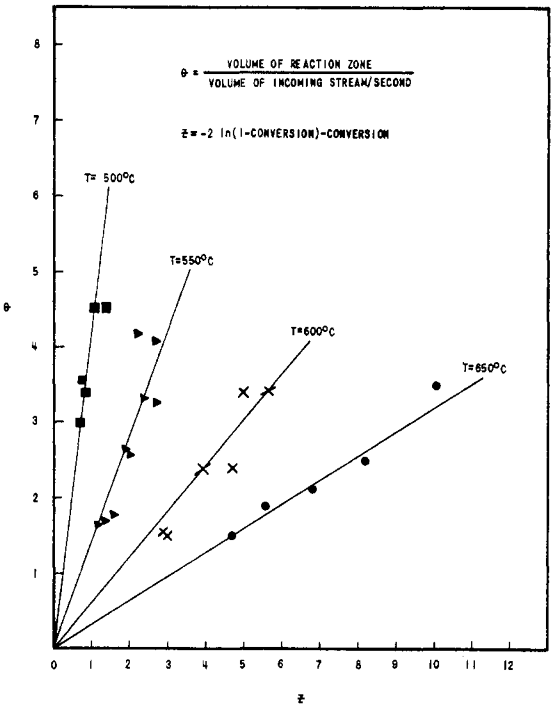

Figure 2. Time θ *vs.* concentration factor, Z

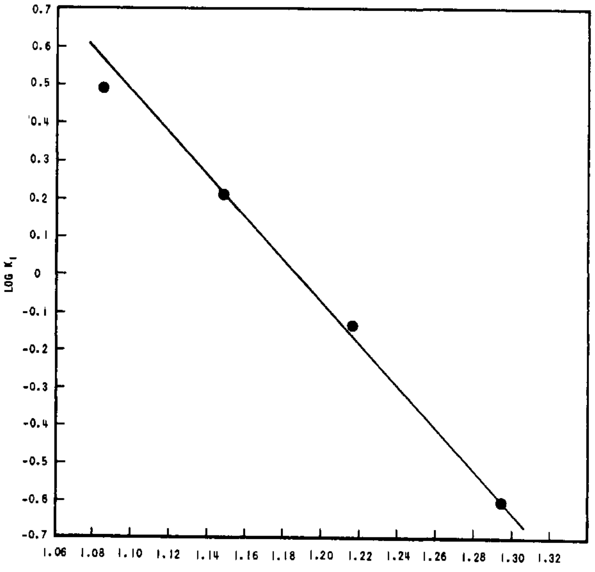

Figure 3. Influence of temperature on rate

This rate equation, found to hold for pumice catalyst, can be used to compare various catalysts at different temperatures, the relative activity being determined by the ratio of space velocities necessary to obtain equal conversions at a given temperature.

ACKNOWLEDGMENT

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