CATALYTIC DEHYDROCHLORINATION OF 1, 2, DICHLOROETHANE TO VINYL CHLORIDE

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ABSTRACT

Catalytic dehydrochlorination of 1, 2, *dichloroethane to vinyl chloride was investigated, employing homogeneous catalysts like carbon tetrachloride, oxygen and chlorine and heterogeneous catalyst Barium chloride on silica gel. It was found that with oxygen, induction period was noticed at low temperatures and low time factor* (V_R/F) *values. Chlorine* (0·5%) *gave optimum yield of* 91% *at* 350°C *and* (V_R/F) *value of* 200. *The solid catalyst* $BaCl_2$ *to* SiO_2 *was found to operate efficiently only at higher temperatures and the life of the catalyst was found to be rather short. The kinetics of the both homogeneous and heterogeneous catalytic reactions could be adequately expressed by a first order irreversible mechanism. The rate controlling step with* $BaCl_2$ *on* SiO_2 *catalyst was found to be the adsorption of dichloroethane over a limited temperature range.*

Key words: Dehydrochlorination; process variables; vinyl chloride.

Vinyl chloride is a monomer, from which one of the most important synthetic resins, polyvinyl chloride, is manufactured. With the development of petrochemical industries, there is a swing from acetylene to ethylene as the raw material. Dichloroethane is produced from ethylene and chlorine in a liquid-phase reaction, employing a suitable catalyst. Mixed feed stock of acetylene and ethylene from pyrolysis of naphtha-fraction is also recommended so as to combine acetylene and ethylene routes of vinyl chloride manufacture.

Dehydrochlorination in the liquid phase by aqueous or alcoholic NaOH or KOH yields about 90% conversion, but is not commercially attractive because of large amounts of alkali consumed. Thermal decomposition of dichloroethane was first studied by Biltz and Kuppers [1] and later by

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Barton [2, 3], Barton and Howlett [4], Baldt and Cremer [5] and Doraiswamy *et al.* [6]. Howlett [7] pointed out the presence of an induction period and established the chain mechanism of reaction involving chlorine atom and 1, 2-dichloroethyl radical as chain carriers. However, thermal decomposition requires higher temperatures and acetylene is produced in large quantities.

A large number of patents are available on heterogeneous catalytic dehydrochlorination, using active carbon, silica gel, pumice, glass powder, sand, bauxite, quartz, chromia, barium chloride, etc. The life of these catalysts is rather short and frequent regeneration steps are required. These difficulties are overcome by using homogeneous catalysts like oxygen, chlorine and carbon tetrachloride. Barton [2, 9] studied oxygen and chlorine induced dehydrochlorination. Lerner *et al.* [8] used 1% Cl_2 as an initiator and arrived at optimum operating conditions by employing experimental design. Michitoshi Kitabatake [9], using CCl_4 as a catalyst, reported the reaction to be of first order with respect to dichloroethane and of second order with respect to carbon tetrachloride.

EXPERIMENTAL

The apparatus (Fig. 1) consists of dichloroethane feeding and metering units, preheater *cum* vaporizer, reactor, product condensers and collection units. The preheater is a 75 cm long, 1 cm i.d. pyrex glass tube, provided with thermowells. The reactor is a 1·9 cm i.d., 30 cm long pyrex glass tube, with two thermowells at the sides. The heating is done electrically and temperatures are controlled by Sunvic energy regulators and autotransformers. The reactor temperature is measured by a Chromel-Alumel thermocouple and is controlled within ± 1° C.

MATERIALS AND ANALYSIS

Commercial 1, 2-dichloroethane was distilled over anhydrous calcium chloride and the fraction boiling at 78° C (at atmospheric pressure of 685 ± 2 mm Hg) having refractive index of 1·4448 (n_D^{20}) was used. All other chemicals used are of BDH analytical grade.

The amount of dichloroethane converted was calculated by estimating the HCl produced using standard titrometric method. Acetylene is estimated by absorbing it in a potassium iodomercurate solution in an Orsat apparatus. For confirming the analysis, vinyl chloride was condensed

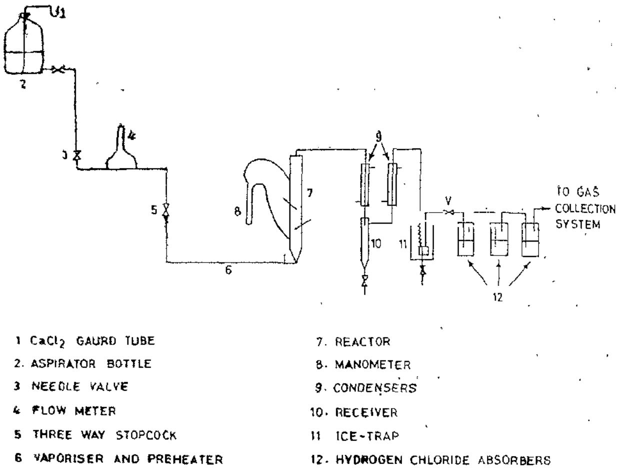


FIG. 1. *Flow diagram of the set-up for dehydrochlorination of dichloroethane to vinyl chloride.*

using dry ice acetone mixture for some runs and analysing by vapour-phase chromatography.

Catalyst Preparation

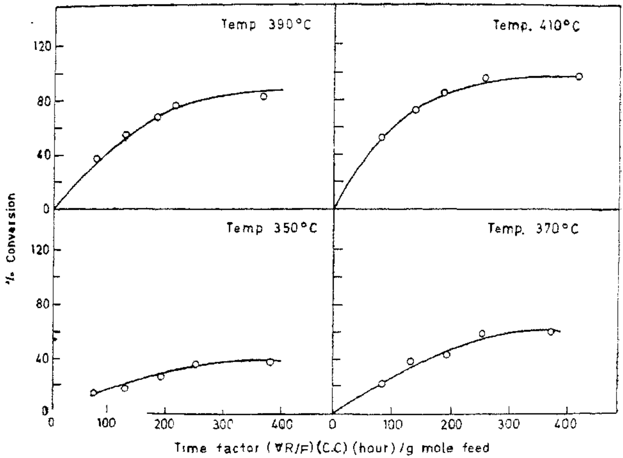
$BaCl_2$ on silica gel catalysts of composition 20 to 80, 30 to 70 and 40 to 60 were prepared by impregnating barium chloride on chromatographic grade of silica gel. Particle size of $-65+100$ Tyler mesh was selected for routine use after confirming that the effectiveness factor for this size to be one. Oxygen and chlorine were tapped from the cylinders and carbon tetrachloride was added to the feed in required proportions.

RESULTS AND DISCUSSION

Catalyst: Carbon Tetrachloride

Three catalyst concentrations, 0·5, 1·0 and 1·5% (v/v) were used. The range of time factor V_R/F and temperature used were 80 to 460 and

350° C to 410° C respectively. It was observed that the conversion of dichloroethane increased with increase in catalyst concentration, however, the difference in the performance with 1·0 and 1·5% catalyst was not appreciable. The data with 1% CCl_4 are presented in Fig. 2. It can be seen from these data, that conversion increases with increase in time factor and the curves, conversion (x) *versus* time factor (V_R/F) tend towards asymptotic values at higher (V_R/F). Conversion increases with increase in temperature but at temperature beyond 410° C, formation of acetylene and deposition of carbon is more.



Catalyst 1.0% (V/V) Carbontetrachloride in feed

FIG. 2. Time factor *vs*. conversion at various temperatures.

Catalyst: *Oxygen*

Oxygen concentrations of 1, 2 and 3 mole % were employed in the temperature and time factor range of 300° to 375° C and 84 to 420 respectively. Optimum conversion was obtained with 3 mole % oxygen as catalyst and the results are presented in Fig. 3. It is observed that the effect of time factor on conversion is similar to that obtained with carbon tetrachloride. The reaction was not studied at temperatures beyond 375° C because of too much deposition of carbon and tarry material.

At temperature of 300° C and 325° C, the conversion obtained was very low up to a time factor of 140. The nature of the (x) *versus* (V_R/F) curves (Fig. 3) indicates the presence of an induction period at lower temperature and (V_R/F) values. At higher temperatures, no induction period was noticed.

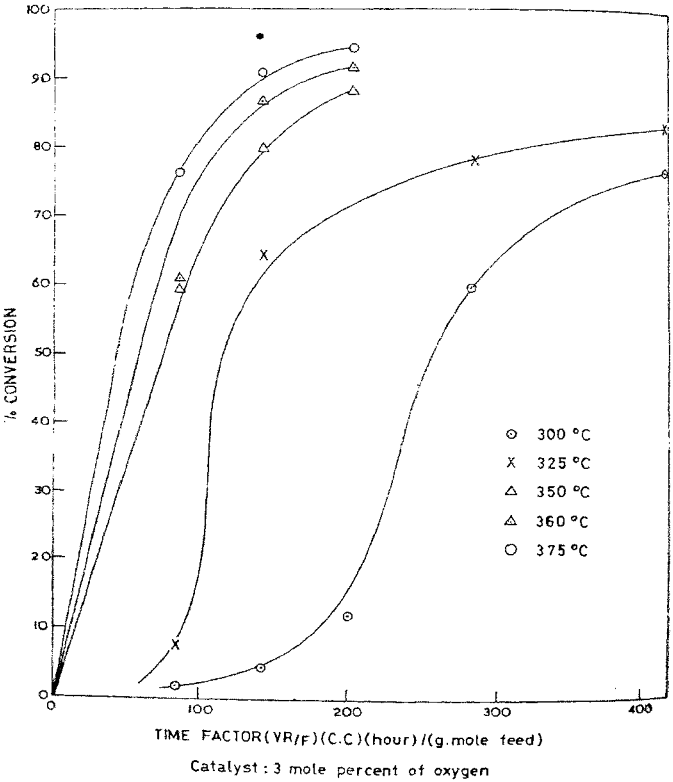


FIG. 3. Time factor *vs.* conversion at various temperatures.

Catalyst: *Chlorine*

Chlorine concentration was varied from 0·25 to 1·5% (by weight) and the range of time factor and temperature employed was 80 to 400″ and 225° C to 350° C respectively. The conversion is found to increase with

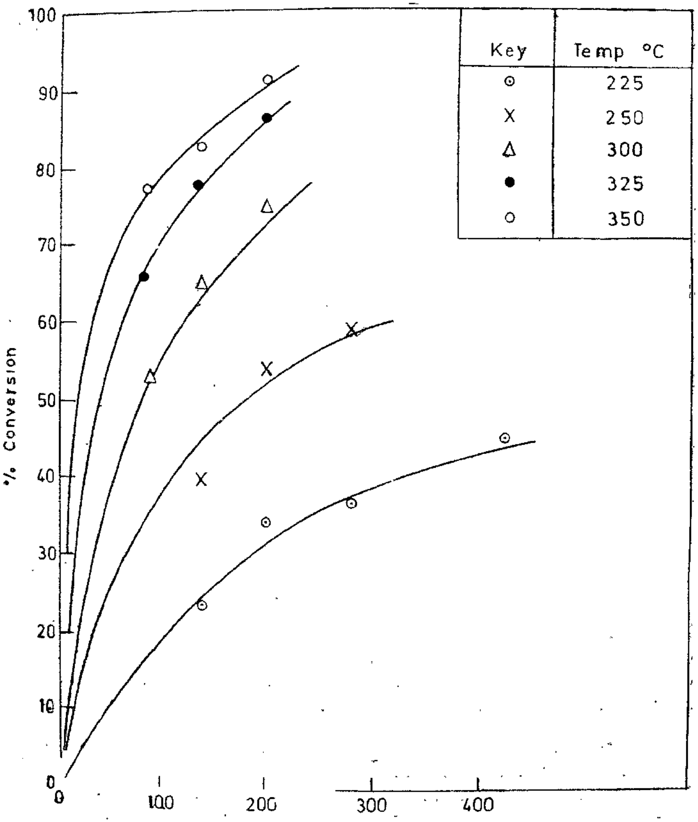


Fig. 4. Time factor *vs*. conversion at various temperatures.

increase in chlorine concentration, but beyond 0·5% Cl_2 concentration, the effect is not significant. The data obtained with 0·5% Cl_2 as a catalyst are given in Fig. 4. The effect of time factor and temperature on conversion is similar to that observed with CCl_4 and O_2. No induction period was observed.

Kinetics

The kinetics of the reaction, $C_2H_4Cl_2 \rightarrow CH_2\,CHCl + HCl$ is studied. The conversion of dichloroethane (x) *versus* (V_R/F) curves were correlated by a third degree polynomial, $x = a\,(V_R/F) + b\,(V_R/F)^2 + c\,(V_R/F)^3$ and the constants a, b and c were calculated by the least square method. The rate of reaction at any (V_R/F) value can be obtained by differentiating the above polynomial with respect to (V_R/F). First-order irreversible rate equation was considered and the following relationship was obtained:

$$k\,(V_R/F) = -\,(RT/P_T)\,[2\ln\,(1-x)+x]. \tag{1}$$

For establishing the linearity between (V_R/F) and the right-hand side of equation (1), the smoothened values of x, *i.e.*, the values of conversion x calculated from the fitted polynomial at various values of (V_R/F) are used. The linearity was found to be statistically significant.

The values of reaction velocity constants obtained from the slopes of the curves are presented in Table I. By the Arrhenius plots (Figs. 5, 6, 7) activation energies and frequency factors were calculated. The reaction velocity constants can thus be expressed as,

$$1\%\ CCl_4 \qquad k = 1{\cdot}714 \times 10^{13}\, e^{-31950/RT}$$

$$3\%\ O_2 \qquad k = 6{\cdot}29 \times 10^{7}\, e^{-13785/RT}$$

$$0{\cdot}5\%\ Cl_2 \qquad k = 8{\cdot}145 \times 10^{7}\, e^{-13428/RT}.$$

The data for oxygen induced dehydrochlorination at 300° C and 325° C were not considered in the calculation of k, as significant induction period was observed. Standard deviation between experimental and calculated conversion values from equation (1) vary between 3·5 to 7·5%.

The presence of 10% by weight of HCl in the feed for chlorine induced reaction has shown no significant effect on the conversion of dichloroethane. The reaction velocity constants obtained with HCl in the feed are presented in Table I. The effect of packing the reactor with pyrex glass rings with 1·5% chlorine as catalyst was studied. With six-fold increase in area over

TABLE I

Reaction velocity constants

No.	Temp. ° C	k (g. mole/c.c. × hr)
	1% CCl_4	
1	350	97·2
2	370	214·2
3	390	472·6
4	410	944·0
	3% O_2	
5	350	947·7
6	360	1161·0
7	375	1459·8
	0·5% Cl_2	
8	225	88·8
9	250	198·5
10	300	536·5
11	325	866·6
12	350	1121·2
	1·5% Cl_2 and 10% HCl in feed	
13	225	70·8
14	250	158·5
15	300	447·6
16	325	775·4
17	350	1180·6
	1·5% Cl_2 packed reactor	
18	225	109·7
19	250	177·6
20	300	559·4
21	325	996·0
22	350	1497·0
	$BaCl_2 : SiC_2$ (30 : 70)	k (lit/hr. × g. cat)
23	425	0·2876
24	450	0·5984
25	475	2·8852
26	500	4·8110

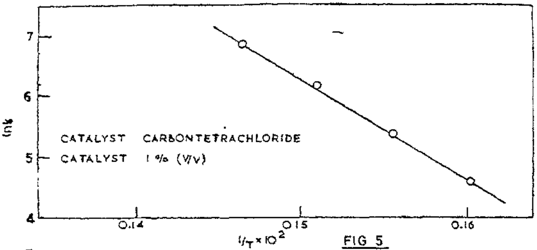


FIG 5

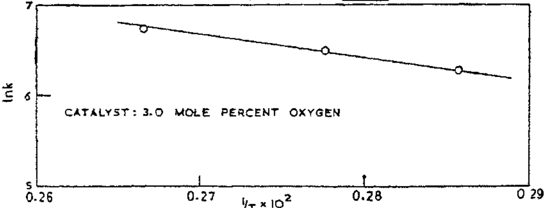
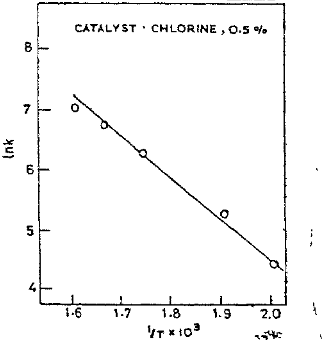


FIG. 6



FIGS. 5–7. Effect of temperature on the rate constant.

the unpacked reactor, it was noticed that very high conversions were obtained initially, which decrease with time and reproducible results could not be obtained. Glass surface acts as a catalyst and the catalytic activity falls with deposition of carbon and tarry material, on the surface. Reproducible results could be obtained only after forty hours of continuous run. It was noticed that higher conversions were obtained in packed reactor. The k values are presented in Table I.

Catalyst: Barium chloride on silica gel

Three catalyst compositions $BaCl_2$ to SiO_2 (20 to 80, 30 to 70 and 40 to 60) were used. The conversion was found to increase with increase in barium chloride concentration. However, the performance with 30 to 70 and 40 to 60 catalysts was not significantly different. The results for catalyst $BaCl_2$ to SiO_2 (30 to 70) are presented in Fig. 8. The range of temperature and time factor (W/F) used was 425° C to 500° C and 10 to 50 respectively. It was found that initially the activity of the fresh catalyst was very high, which falls rapidly during the first three hours. Even after regeneration with oxygen at 450° C for eight hours, the initial activity could not be obtained. However, the regenerated catalyst yields reproducible results and maintains its activity for more than four hours. The results presented in Fig. 8 are those obtained with regenerated catalyst during constant activity period.

The conversion increases with increase in time factor and the curves conversion *versus* time factor become asymptotic at higher W/F values. Increase in temperature causes the increase in conversion.

Kinetics

Following the treatment used for homogeneous catalysts, it was noticed that equation (1) adequately represents the data. The values of reaction velocity constants are presented in Table I. The reaction velocity constant can be expressed as,

$$k = 8 \cdot 366 \times 10^{12}\, e^{-42958/RT}.$$

Standard deviation between experimental and calculated conversion values is 7%.

Hougen-Watson Reaction Mechanism

In order to evaluate the extent of internal and external diffusion in the reactor system, experiments were carried out with $-65+100$ and $-100+150$ Tyler mesh catalyst size and with two bed heights using 10 and 20 gm of catalyst. The conversion values with $-65+100$ and $-100+150$ mesh size were similar under identical operating conditions, indicating negligible internal diffusion resistance. Similarly, almost same

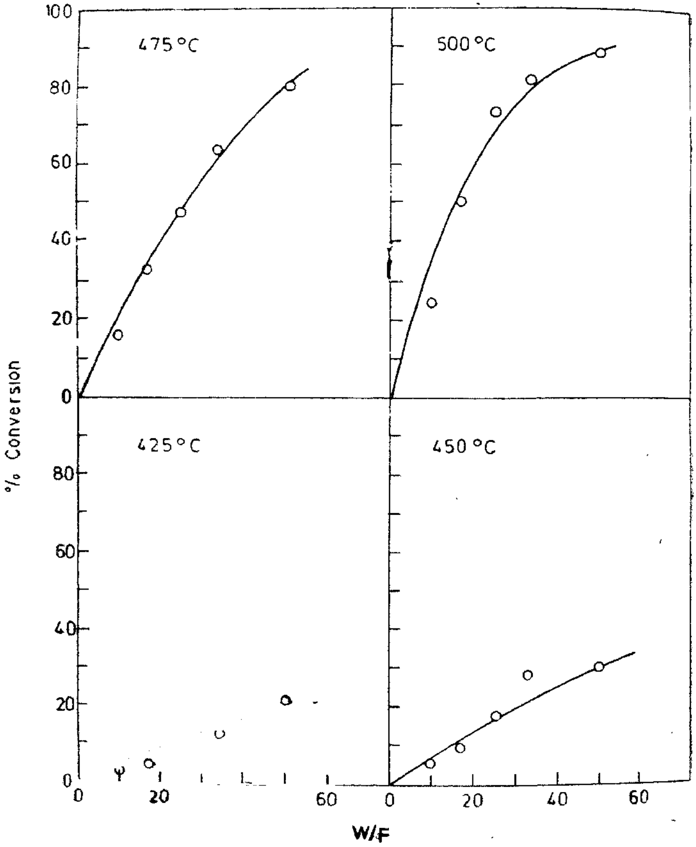


FIG. 8. Effect of time factor on conversion.

conversions were obtained with two different bed heights at equal W/F and temperature values, thus showing the absence of external diffusion controlling step in the range of time factor employed.

When various mechanisms and rate controlling steps were tried, single site, adsorption of dichloroethane was found to be the rate determining step. The apparent reaction velocity constant k_S and the adsorption equilibrium constant K_S can be expressed as,

$$k_S = 1 \cdot 259 \times 10^{13} \, e^{-50010/RT}$$

and

$$K_S = 4 \cdot 217 \times 10^{-5} \, e^{-12390/RT}$$

Following rate expression can thus be used,

$$r = \frac{1 \cdot 259 \times 10^{13} \, e^{-50010/RT} \left[P_A - \frac{P_R \, P_S}{K} \right]}{[1 + 4 \cdot 217 \times 10^{-5} \, e^{+12390/RT} \, P_S]} \tag{2}$$

The standard deviation between the experimental and calculated rates by equation (2) is 5·2%. However this expression is found valid in the temperature range of 450° C – 500° C only.

Catalyst Performance

With $BaCl_2$ on silica gel catalyst, 88·5% conversion was obtained at 500° C and W/F value of 50. Very little conversion was noticed at temperatures below 425° C. On the other hand, homogeneous catalysts could give satisfactory performance in a lower temperature range. Oxygen induced dehydrochlorination exhibits induction periods at lower temperatures. Chlorine, with 0·5% concentration, yields conversion of 90% at 350° C and (V_R/F) value of 200. Hence chlorine seems to be the most efficient catalyst for this dehydrochlorination reaction.

NOMENCLATURE

a	Constant,
b	Constant,
c	Constant,
E	Activation energy, cal/g. mole,
F	Feed rate, moles/hr,
k	Reaction velocity constant,
k_S	Apparent reaction velocity constant,
K_S	Adsorption equilibrium constant for hydrogen chloride,
P_A	Partial pressure of dichloroethane, atm,

P_S	Partial pressure of HCl atm,
P_T	Total pressure atm,
R	Gas constant,
T	Absolute temperature, °K,
V_R	Reactor volume, c.c.,
W	Weight of catalyst, gms.

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