JOURNAL OF CATALYSIS 32, 466–469 (1974)

The Catalytic Decomposition of 1,2-Dichloroethane with Activated Carbon Catalysts

J. J. PRINSLOO, P. C. VAN BERGE, AND J. ZLOTNICK

Department of Chemistry, Rand Afrikaans University,
Johannesburg, South Africa

Received April 13, 1973

The catalytic decomposition of 1,2-dichloroethane to vinyl chloride and hydrogen chloride was studied with three activated carbon catalysts. The order of the reaction was found to be 0.7 and the activation energies were 142, 122, and 119 kJ/mole. The results were interpreted by a mechanism which included adsorbed activated 1,2-dichloroethane complex on the surface of the catalyst.

INTRODUCTION

Many patents have appeared on the catalytic activity of carbon for the decomposition reaction of 1,2-dichloroethane to vinyl chloride and hydrogen chloride (*1*). However, only a few articles have been published on the kinetics of this process (*2*), and there is little known of the steps participating in the reaction. In the present work the kinetics of the reaction have been studied.

METHODS

The kinetic experiments were carried out with a batch reactor and a continuous flow reactor. The batch reactor was a Pyrex glass vessel of 40 cm^3 connected to a conventional vacuum system. The rate of the reaction was determined by measuring the pressure with a mercury manometer as a function of time.

The continuous flow reactor was constructed from Pyrex glass. The 1,2-dichloroethane was introduced into the reactor tube according to a method described by Schwab and Knözinger (*3*). The reactor tube (diameter 25 mm) was packed with 8 gm of glass particles (diameter 20–35 mesh, U. S.) to preheat the reactor gas and 1.5 g of a catalyst bed. The effluent gas was successively passed through a cooled trap (0°C) to remove condensable 1,2-dichloroethane, a sodium hydroxide solution to remove hydrogen chloride, a drying tube, a sample valve, and a soap-bubble flowmeter. The sample valve was connected to a Philips gas chromatograph (type PV 4000). The chromatographic columns (length 1.9 m, outer diameter 5 mm) were packed with 60–80 mesh (U. S.) Chromosorb and SE 30 as a stationary phase. Both reactors were thermostatted with Ether temperature regulators with an accuracy of 0.5°C and the reactor temperatures were measured with chromel/alumel thermocouples mounted in glass wells in order to measure the temperature in the center of the reactors.

The surface areas of the catalysts were determined using the apparatus described by Lippens, Linsen, and De Boer (*4*) and calculated by means of the BET-method.

The catalysts used were a commercial activated charcoal (Riedel-de Haën) mortarized to 20–30 mesh (U. S.) (I) and two carbons which were prepared from Hullets refined cane sugar. The preparation of these latter carbons was carried out by an adaptation of the method of Smith and Mooi (*5*) to give a maximum yield of low ash carbon powder. The powder was pressed to tablets, fired at 800°C, and mortarized to particle sizes of 20–30 mesh

(U. S.). The catalysts were prepared from these carbon particles by activation at 950°C with air (2 hr) and CO_2 (2 hr) (II) or with air (5 hr) and CO_2 (5 hr) (III).

RESULTS

The influence of the pressure of 1,2-dichloroethane and of the temperature on the rate of the reaction was determined with the flow reactor. In all the experiments the conversions did not exceed 1.5% and it was verified that within these limits the differential rates of the reaction were measured. Furthermore it was ascertained that under the experimental conditions the thermal decomposition could be detected only at temperatures higher than 380°C which is well above the temperature range of the present catalytic study.

Using the three catalysts, the order of the reaction with respect to 1,2-dichloroethane was determined in the temperature range 266°–356°C. For each of the catalysts the order of the reaction was within experimental error shown to be independent of temperature and the average value of 0.7 was obtained for the three catalysts. Some of the results are shown in Fig. 1.

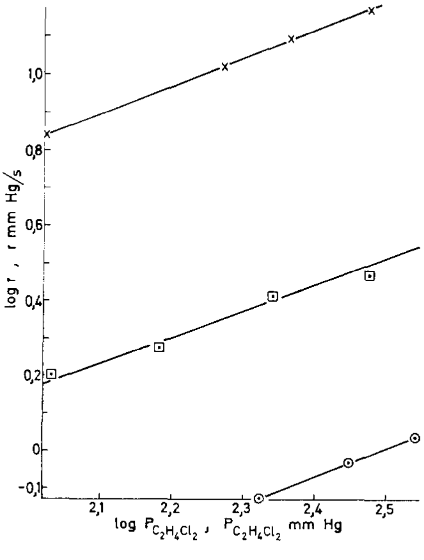

FIG. 1. Experimental determination of the kinetic order: (○) catalyst I at 537 K, $n = 0.74$, (⊡) catalyst II at 561 K, $n = 0.62$, and (×) catalyst III at 602 K, $n = 0.72$.

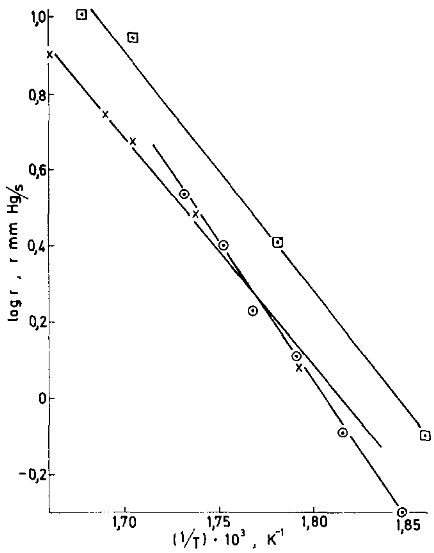

FIG. 2. Linear relationship of log r with $1/T$: (○) catalyst I, (⊡) catalyst II, and (×) catalyst III.

The activation energies were determined in the temperature range 266°–356°C at constant 1,2-dichloroethane pressure (Fig. 2). A summary of the results are shown in Table 1.

Experiments were carried out to determine whether the reaction products, viz., hydrogen chloride and vinyl chloride, had any influence on the rate of the reaction. This was most easily done by means of a batch reactor, measuring the pressure as a function of time with mixtures made up of helium and a product with the same amount of 1,2-dichloroethane at the same reactor temperature of each of the products successively. From the results (Fig. 3) it can be concluded that, to a good approximation, the rate of the reaction is in-

TABLE 1
SURFACE AREAS AND ACTIVATION ENERGIES OF CARBON CATALYSTS

Catalyst	Surface area (m^2/g)	Activation energy (kJ/mole)
I	1100	142
II	533	122
III	727	119

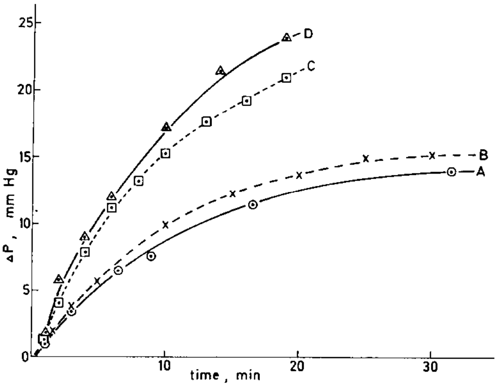

FIG. 3. Influence of the reaction products, hydrogen chloride and vinyl chloride, on the rate of the reaction: (A) 60 mm Hg 1,2-dichloroethane + 150 mm Hg helium at 370°C, (B) 63 mm Hg 1,2-dichloroethane + 366 mm Hg vinyl chloride at 371°C, (C) 83 mm Hg 1,2-dichloroethane + 299 mm Hg hydrogen chloride at 365°C, and (D) 89 mm Hg 1,2-dichloroethane + 136 mm Hg helium at 365°C.

dependent of the presence of hydrogen chloride and vinyl chloride in the reactor. It was not necessary, therefore, to repeat these experiments with the flow reactor.

DISCUSSION

The results obtained from the decomposition of 1,2-dichloroethane with three activated carbon catalysts can be fitted to the following rate equation:

$$r = kP_{C_2H_4Cl_2}{}^{0.7}$$

where $P_{C_2H_4Cl_2}$ is the pressure of 1,2-dichloroethane. Assuming that the activated complex is adsorbed $C_2H_4Cl_2{}^{*\ddagger}$, the following effective equilibrium can be postulated (*6*, *7*):

$$0.7\ C_2H_4Cl_2(g) + 0.3\ C_2H_4Cl_2{}^* + 0.7^* \rightleftharpoons C_2H_4Cl_2{}^{*\ddagger}, \quad (1)$$

where * represents an adsorption site. Following this method, where

$$k = \kappa \frac{\mathbf{k}T}{\mathbf{h}} K^{\ddagger},$$

$$K^{\ddagger} = e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S^{\ddagger}/R},$$

is the equilibrium constant of Eq. (1), and

$$\Delta S^{\ddagger} = 0.7[S^{\ddagger} - S^{\circ}_{C_2H_4Cl_2(g)}]$$
$$\Delta H^{\ddagger} = E - RT. \quad (2)$$

E is the experimentally determined activation energy.

When $(S^{\circ}_{C_2H_4Cl_2(g)} - S^{\ddagger})$ is taken as the translational entropy of 1,2-dichloroethane, calculated values of the activation entropies, $\Delta S^{\ddagger}_{\text{calc}}$, may be obtained from:

$$\Delta S^{\ddagger}_{\text{calc}} = 0.7 S^{\circ}_{C_2H_4Cl_2(g)}\ \text{(translational)},$$

and these can be compared with the $\Delta S^{\ddagger}$ values obtained from the rate constant *k*. The results are summarized in Table 2. It is apparent that there is a good agreement between the $\Delta S^{\ddagger}$ and $\Delta S^{\ddagger}_{\text{calc}}$ values for the catalysts II and III.

From this it may be concluded that the activated complex is 1,2-dichloroethane adsorbed on the surface. The following steps can be proposed for the reaction:

$$C_2H_4Cl_2(g) + {}^* \rightleftharpoons C_2H_4Cl_2{}^* \quad (3)$$
$$C_2H_4Cl_2{}^* \rightleftharpoons C_2H_4Cl_2{}^{*\ddagger} \rightarrow C_2H_3Cl + HCl.$$

Assuming the Langmuir isotherm, the following equation for the rate per unit of surface area is obtained:

$$r = \frac{k_2 L b P_{C_2H_4Cl_2}}{1 + bP_{C_2H_4Cl_2}}$$

TABLE 2
RATE PARAMETERS FOR THE DIFFERENT CATALYSTS

Catalyst	Temperature (°K)	k (molecules/s · sites)	$\Delta S^{\ddagger}$ (J/degree · mole)	$\Delta S^{\ddagger}_{\text{calc}}$ (J/degree · mole)	A	A_{calc}
I	544.6	5.7×10^{-6}	−79.1	−124.4	8.7×10^{8}	1.6×10^{4}
II	561.2	5.9×10^{-2}	−128.5	−125.5	8.9×10^{6}	1.4×10^{4}
III	596.4	2.0×10^{-4}	−130.0	−126.4	13.5×10^{6}	0.7×10^{4}

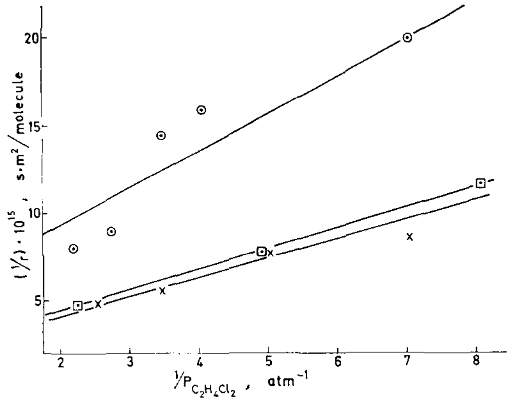

FIG. 4. Linear relationship of $1/r$ with $1/P_{C_2H_4Cl_2}$: (⊙) catalyst I, at 565.0 K, (×) catalyst II at 562.2 K, and (⊡) catalyst III at 564.4 K.

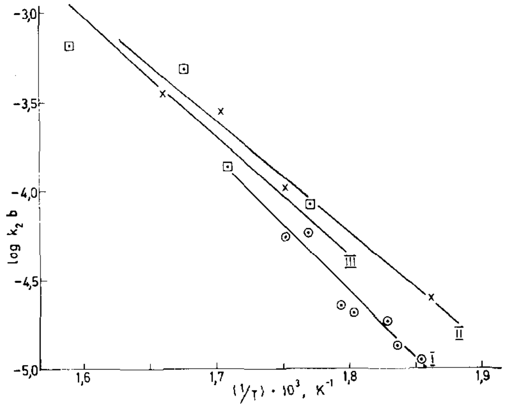

FIG. 5. Linear relationship of log k_2b with $1/T$: (⊙) catalyst I, (×) catalyst II, and (⊡) catalyst III.

where b is the adsorption coefficient of Eq. (3) and where k_2 is the rate constant of the rate determining step. In agreement with this equation linear plots of $1/r$ against $1/P_{C_2H_4Cl_2}$ were obtained. An example of this is shown in Fig. 4. From the slopes, values of k_2Lb were obtained and assuming $L = 10^{19}$ sites/m², the product k_2b was calculated.

The values of k_2b, obtained from experiments at various temperatures, could be fitted to:

$$\ln k_2b = \ln A - \frac{E'}{RT},$$

by plotting log k_2b against $1/T$, (see Fig. 5) calculating E' from the slope and estimating the order of magnitude of A from the intercept.

From

$$A_{\text{calc}} = \kappa \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S^{\ddagger}/R},$$

and taking $\kappa = 1$ and $\Delta S^{\ddagger}$ equal to the translational entropy of 1,2-dichloroethane (g), A_{calc} is obtained.

It is apparent from Table 2 that there is a large deviation between the calculated and experimental preexponential factors obtained from experiments with catalyst I, whereas a satisfactory agreement is obtained with catalysts II and III. From this and the $\Delta S^{\ddagger}$ values, it may be concluded that the proposed model agrees with the kinetic results obtained with the catalysts prepared in the laboratory, but that the reaction probably proceeds by another mechanism with the commercial activated carbon (I).

REFERENCES

1. OKAMOTO, K., TANAKA, N., ADACHI, K., AND SHINGU, H., *Bull. Chem. Soc. Japan* **39** (7), 1522 (1966).
2. WALTER, C. R., *J. Chem. Eng. Data* **5**(4), 468 (1960).
3. SCHWAB, G. M., AND KNÖZINGER, H., *Z. für physikalische Chemie Neue Folge* **37**, 230 (1963).
4. LIPPENS, B. C., LINSEN, B. G., AND DE BOER, J. H., *J. Catalysis* **3**, 32 (1964).
5. SMITH, R. N., AND MOOI, J., *J. Phys. Chem.* **59**, 814 (1955).
6. SCHUIT, G. C. A., AND VAN REIJEN, L. L., *Adv. in Catalysis* **10**, 242 (1958).
7. GOLODETS, G. I., AND ROITER, V. A., *Kinet. Catal.* **4**, 153 (1963).