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The Catalytic Dehyrochlorination of 1, 2-Dichloroethane on Active Carbon in the Presence of Some Hydrocarbons

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The catalytic pyrolysis of 1, 2-dichloroethane on active carbon, carried out at 300 and 400°C in the presence of toluene, benzene and *n*-hexane, resulted predominantly in ethylene instead of vinyl chloride, which is known in the literature as the major pyrolysis product of the titled compound; the pyrolysis rates were suppressed by these hydrocarbons. These results have been explained by assuming a radical-chain mechanism similar to that suggested for the "homogeneous" pyrolysis of this compound. The chain length derived from the proposed mechanism has been estimated to be 20 to 50.

A number of studies concerned with the mechanism of the homogeneous pyrolysis of 1, 2-dichloroethane have been reported in recent years.[1] In contrast, little work has been done with the catalytic mechanism of the pyrolysis on active carbon, although the use of active carbon for the pyrolytic manufacture of vinyl chloride from 1, 2-dichloroethane has been extensively investigated.[2] During the course of our study of the active carbon catalyst for the preparation of vinyl chloride from 1, 2-dichloroethane,[2g,h] we felt it desirable to carry out several experiments in order to clarify the mechanistic nature of this catalytic reaction; in this paper we will report on some of the results, which support unambiguously the mechanism including radicals as the intermediates of the reaction on the surface of the active carbon catalyst.

The dehydrochlorination was carried out by means of a flow method at 300 and 400°C in the presence of hydrocarbons, such as *n*-hexane, toluene and benzene. 1, 2-Dichloroethane or a mixture of it with the hydrocarbons was fed to an integral reactor filled with the active carbon catalyst[2h] in a fixed bed. At the exit of the reactor the gaseous effluent entered a water-cooling condenser and ice-water trap; then hydrogen chloride was trapped by an absorption bottle containing aqueous sodium hydroxide, and finally the non-condensables were collected in a gas holder. The composition of the condensates and gases were analyzed by gas-liquid chromatography. The results are shown in Table I.

In the absence of hydrocarbons, 1, 2-dichloroethane decomposed almost completely under the reaction conditions employed. At the reaction temperatures of 300 and 400°C, the percentage conversion amounted, respectively, to 94.5 and 99% at the flow rate of 0.22 cc. of liquid 1, 2-dichloroethane per 1 cc. of active carbon per hour (Runs 1 and 2).

By the addition of hydrocarbons, the decomposition of 1, 2-dichloroethane was considerably inhibited. The addition of 4 mol. of toluene reduced the conversion percentage of 1, 2-dichloroethane from 94.5 to 8.5% at 300°C (Run 4). 1, 2-Dichloroethane mixed with 3 mol. of *n*-hexane gave a 50% conversion at 402°C (Run 7), whereas pure 1, 2-dichloroethane gave a 98% conversion at 380°C at a comparable flow rate (Run 3).

Furthermore, we found that the nature of the pyrolysis products was dramatically changed by the addition of these hydrocarbons. In the absence

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TABLE I. CATALYTIC DEHYDROCHLORINATION OF 1,2-DICHLOROETHANE ON ACTIVE CARBON

Run No.	Feed: 1,2-Dichloroethane mole	Feed: Hydrocarbon mole	Temp. °C	Vol. of act. carbon cc.	Liquid space velocity of 1,2-dichloroethane hr^{-1}	HCl% based on 1,2-dichloroethane	Conversion%[a] of 1,2-dichloroethane	Distribution, %: Ethylene	Distribution, %: Vinyl chloride	k[b] sec^{-1}
1	0.162	none	300	30	0.22	98.0	94.5	1.7[c]	98.3	0.154
4	0.200	Toluene 0.800	300	30	0.22	14.1	8.5	94.8[c]	4.7	0.0034
2	0.318	none	400	30	0.22	101	99.0	1.0[c]	99.0	0.293
5	0.200	Benzene 0.910	400	30	0.22	102	82.3	16.9[d]	81.7	0.109
6	0.200	*n*-Hexane 0.800	400	30	0.22	188	98.3	95.7[e]	3.1	0.348
3	0.317	none	380	40	1.25	98.0	98.0	0.5[c]	99.0	1.37
7	0.095	*n*-Hexane 0.300	402	10	1.00	98.0	50.0	90.5[c]	6.0	0.200

a) Calculated from the amount of the recovered 1,2-dichloroethane.
b) Total rate constant, calculated from the conversion % of 1,2-dichloroethane and the composition of the products by using the equation similar to that cited by Barton.[1a]
c) For the other minor products see text.
d) Acetylene 0.05%; benzene, recovered, 98.5%.
e) Acetylene 0.3%; ethane, 0.8%; ethyl chloride, 0.1%; hexane, recovered, 94.0%.

of the hydrocarbons, pure 1, 2-dichloroethane gave vinyl chloride exclusively (more than 98% of the composition of the product); at most 2% of ethylene was found as a minor product (Runs 1, 2 and 3). A gas chromatographical examination of the other minor components reveales the presence of small amounts of ethyl chloride (about 0.1% in composition), *cis*-1, 2-dichloroethylene (0.05%), 1, 1-dichloroethane (0.02%), *trans*-1, 2-dichloroethylene (0.02%) and vinylidene chloride (0.01%). In the presence of the hydrocarbons, however, the major product was not vinyl chloride, but, rather, ethylene (more than 90% of the composition of the product). For instance, in the decomposition of 1, 2-dichloroethane mixed with 4 mol. of toluene, a mixture consisting of 94.8% ethylene, 4.7% vinyl chloride, and a small amount of other, minor products, such as ethyl chloride (about 0.04%) and acetylene (at most 0.01%), was obtained at 300°C (Run 4). More than 97.4% of the toluene was recovered; about 0.2% of it was then converted to *trans*-stilbene. In another example at 400°C (Run 7), a mixture of *n*-hexane and 1, 2-dichloroethane (3 : 1 by mole) gave a gaseous product containing 90% ethylene as a major product, 6% vinyl chloride, 0.04% acetylene, 0.54% ethane, and, at most, 0.01% ethyl chloride; more than 90% of the added *n*-hexane was recovered.

On the basis of the above results, we may suggest that the pyrolysis of 1, 2-dichloroethane on the active carbon catalyst proceeds by a radical chain mechanism similar to that suggested for the "homogeneous" dehydrochlorination.[1a,b] Namely, the homogeneous pyrolysis is also inhibited in the presence of these hydrocarbons,[1a] and the chain propagation can be initiated mainly at the treated, i. e., carbon-coated, walls.[1f,g]

Thus, for this catalytic dehydrochlorination, the initiation step may be formulated as:

$$ClCH_2CH_2Cl + \text{Active carbon} \xrightarrow{k_1} Cl + \cdot CH_2CH_2Cl$$

or $$\cdot CH_2CH_2Cl + \text{Active carbon} \xrightarrow{k_2} Cl + CH_2{=}CH_2$$

In the absence of the hydrocarbons, the chain propagation would proceed in the same manner as in the homogeneous pyrolysis, as is indicated below:

$$Cl + ClCH_2CH_2Cl \xrightarrow{k_3} HCl + Cl\dot{C}HCH_2Cl$$
$$Cl\dot{C}HCH_2Cl \xrightarrow{k_4} Cl + ClCH{=}CH_2 \quad \text{Chain}$$
$$Cl + Cl\dot{C}HCH_2Cl \xrightarrow{k_5} ClCH_2CHCl_2 \quad \text{Termination}$$

The further pyrolytic decomposition of 1, 1, 2-trichloroethane would form 1, 1-dichloroethane, *cis*- and *trans*-1, 2-dichloroethylene; these compounds have been identified in the minor reaction products.

In the presence of the hydrocarbons, the chain-carrying chlorine atom would be destroyed by the hydrogen donation from these hydrocarbons. As a result, the formation of vinyl chloride would be suppressed; accordingly, the decomposition of a 2-chloroethyl radical to ethylene would become preponderant:

$$Cl + RH \xrightarrow{k_6} HCl + \cdot R\downarrow \quad \text{Termination}$$

This termination of the radical-chain by the

hydrocarbons cansequently causes a decrease in the total rate of the conversion of 1, 2-dichloroethane. This is illustrated by a comparison of the following total rate expressions for 1, 2-dichloroethane alone and for its mixture with the hydrocarbons.

In the absence of the hydrocarbons:

$$-\frac{d(EDC)}{dt}=\left(\frac{2k_1k_3k_4}{k_5}\right)^{1/2}(EDC)+k_1(EDC) \quad (1)$$

In the presence of the hydrocarbons:

$$-\frac{d(EDC)}{dt}=\left\{\left(\frac{k_6k_4}{2k_5}\right)^2(RH)^2+\frac{2k_1k_3k_4}{k_5}(EDC)^2\right\}^{1/2}-\frac{k_4k_6}{2k_5}(RH)+k_1(EDC) \quad (2)$$

where (EDC) and (RH) are, respectively, the effective concentrations of 1, 2-dichloroethane and of the hydrocarbon on the surface of the active carbon; it is assumed that the reaction proceeds in the adsorbed layer and that the rate of adsorption and desorption are rapid as compared to the reaction rates.

If the above reaction sequence is accepted and the second term of Eq. 1 is neglected compared to the first, it is possible to compute the chain length in the propagation stage for this catalytic dehydrochlorination:

$$\text{Chain length}=\frac{k_3(EDC)}{k_5(ClCHCH_2Cl)}=\frac{1}{2}\cdot\left(\frac{2k_1k_3k_4}{k_5}\right)^{1/2}\cdot\frac{1}{k_1}=\frac{1}{2}\cdot\frac{d(\text{Vinyl Chloride})}{d(\text{Ethylene})}=\frac{1}{2}\cdot\frac{(\text{Vinyl Chloride }\%)}{(\text{Ethylene }\%)} \quad (3)$$

Therefore, the chain length at temperatures ranging from 300 to 400°C is estimated to be 20 to 50 from the data in Runs 1 and 2.

Experimental

Apparatus. — All the reactions were studied by streaming the vapor of 1, 2-dichloroethane* or its mixture with hydrocarbons at a constant rate through a catalyst bed in a hard-glass tube, 1.9 cm. in internal diameter. The tube was 70 cm. in length of which 50 cm. were heated in an electric furnace inclined at a slight angle to the horizon. An active carbon catalyst[2h] (manufactured by the Takeda Chemical Ind. Co., Ltd., Osaka; 15 g.; 40 cc. bulk volume; 8 to 12 mesh) was supported by a plug of glass wool. A glass thermocouple well (7 mm. o. d.) ran through the center of the catalyst bed, which was 20 cm. long for 40 cc. of the catalyst, and was situated in the center portion of the furnace. The bed temperature was uniform along its length to ±2°C (300 to 400°C). The 10 cm. portion of the tube immediately in front of the catalyst served as an evaporator and a preheater. 1, 2-Dichloroethane, placed in a graduated liquid feed tube with a capillary outlet tubing fitted at the top, was forced into a reaction vessel by feeding mercury from a dropping funnel into the tube at a constant rate. The delivery rates (liquid space velocity) of 1, 2-dichloroethane were 0.22 and 1.25 (cc. per cc. of the catalyst per hr.). In the case of the latter liquid space velocity, the bed temperature and the temperature at the preheater portion were kept about 10°C higher than the reaction temperature just before the feeding in of 1, 2-dichloroethane, because the endothermicity of this pyrolysis causes a temperature depression at such a high feeding rate. The temperature of the inlet of the bed was 5 to 10°C lower than that of the outlet. Thus, the reaction temperature was measured at the midpoint of the bed. At the exit of the reactor the gas flow entered a series of tared product traps, i. e., a water-cooling condenser fitted with a graduated cylinder, a graduated trap at 0°C (ice water), and a graduated gas-holder filled with saturated aqueous sodium chloride. In the case of the run for analysis of the minor reaction products, the gas-holder was replaced with another trap at −70°C (solid carbon dioxide - methanol). Except in this analysis run, hydrogen chloride was caught by means of an absorption bottle filled with 2—5 N sodium hydroxide provided between the gas-holder and the other traps. Before each run, the air in the free space was replaced by nitrogen, and after the run the gaseous products in the free space were transfered to the condensers or traps by a nitrogen stream.

Product Analysis.—The reaction products were analyzed gas chromatographically with a Perkin-Elmer model 154B Vapor Fractometer. The column for chlorine compounds was a Perkin-Elmer column A (2 m. long with diisodecyl phthalate as the liquid). The retention times for ethyl chloride, 1, 1-dichloroethane, 1, 2-dichloroethane, 1, 1, 1-trichloroethane, 1, 1, 2-trichloroethane, 1, 1, 2, 2-tetrachloroethane, vinyl chloride, vinylidene chloride, *trans*-1, 2-dichloroethylene, *cis*-1, 2-dichloroethylene and 1, 2-dichloropropane were, respectively, 1.7, 6.1, 13.0, 9.4, 54, 217, 1.2, 3.0, 4.7, 8.8, and 18.5 min., as determined at 64°C with hydrogen as a carrier gas and at a flow rate of 55 cc. per min. The column for hydrocarbon gases was a Perkin-Elmer column J (2 m. long, with silica gel as the solid). The retention times for ethane, ethylene, acetylene and vinyl chloride were, respectively, 3.6, 5.5, 13.6, and 51 min., as determined at 84°C with helium as the carrier gas and at a flow rate of 50 cc. per min.

After the run the aqueous sodium hydroxide in the absorption bottle was neutralized with nitric acid and the chlorine content was determined by the Mohr method. The condensates in the water-cooling condenser were distilled, and most of the hydrocarbons were recovered (Runs 4—7). In the run with toluene (Run 4), a small amount of the distillation residue (a solid) gave 0.20 g. of *trans*-stilbene, m. p. 120—122°C, after the recrystallization from ethanol. The identity of this with authentic *trans*-stilbene was established by comparing the infrared spectra taken with a Shimadzu model IR-27.

* The material contained as impurities 0.029% 1, 1-dichloroethane, 0.023% 1, 2-dichloropropane, and 0.058% 1, 1, 2-trichloroethane (analysis by gas chromatography).