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GAS CHROMATOGRAPHIC STUDIES OF VINYL CHLORIDE IN AIR BY CATALYTIC HYDROGENATION TO ETHYL CHLORIDE

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SUMMARY

In order to investigate the amount of vinyl chloride in air, the hydrogenation of vinyl chloride to ethyl chloride is used. This method of determination is preferable to the other methods described in the literature because: (a) it proves that only vinyl chloride goes through hydrogenation by its displacement to the ethyl chloride peak in the chromatogram; (b) the actual amount of vinyl chloride can be obtained in the case of superimposed or interfering peaks (*e.g.*, various gases contained in air samples), either by calculating the ethyl chloride peak area or by the reduction of the peak area in the region of the same retention time as the vinyl chloride peak in the related chromatogram.

In this study various kinds of catalysts for hydrogenation purposes at temperatures ranging from -20 to 250° have been used. Among the catalysts used palladium gives the best results at low temperature.

INTRODUCTION

In recent years vinyl chloride monomer (VCM) has been shown to be a carcinogenic agent and some cases of angiosarcoma (cancer of the liver)¹ are seen in the people who work in poly(vinyl chloride) (PVC) production plants and factories. The determination of vinyl chloride in the environment of such factories and its threshold limits has become obligatory in some countries². One of the problems of determining vinyl chloride^{3,4} present in minute amounts (ppm) is the interference from other gases in the air. This interference may be eliminated by the catalytic hydrogenation⁵ of vinyl chloride to ethyl chloride.

In this study the catalytic hydrogenation of vinyl chloride to ethyl chloride was examined using various catalysts such as Pt, Pd, Ni, Cu and Cr at various temperatures.

EXPERIMENTAL

Reagents

Vinyl chloride was obtained from Schuchardt, Munich, G.F.R., and ethyl

chloride from Henning, Walldrof, Baden, G.F.R. The chromatographic support material was Porapak QS (80–100 mesh) (Waters Assoc., Milford, Mass., U.S.A.) and the catalysis supports were Chromosorb P AW (60–80 mesh) (Varian Aerograph, Walnut Creek, Calif., U.S.A.) and glass beads (45–60 mesh).

Apparatus

A Varian Aerograph Model 2800 gas chromatograph equipped with a flame-ionization detector was used. Operating conditions: carrier gas, hydrogen (5 ml/min) plus helium (20 ml/min); air flow-rate, 300 ml/min; electrometer, $10^{-9} \times 128$, 256 or 512 A/mV and $10^{-10} \times 64$ A/mV for pure vinyl chloride, $10^{-9} \times 1$ or 4 A/mV for 4500 ppm and $10^{-12} \times 1$ or $10^{-11} \times 2$ A/mV for 20 ppm of standard. The coiled stainless-steel column (3 ft. \times 1/8 in.) was packed with Porapak QS (80–100 mesh) and conditioned at 230° with helium at a flow-rate of 15 ml/min for 48 h. Temperatures: column, 100°; injector, 250 to 100°; detector 150°; catalysis unit, -20 to 50°. A Model KT 33 constant-temperature refrigerating water-bath circulator (Haake, Karlsruhe, G.F.R.) was used.

Catalysis unit. The injector block of the gas chromatograph was used as the catalysis unit at temperatures higher than 50°. The injector tube was packed with 1% of a metal impregnated as its nitrate or chloride salts on 0.45 g of the Chromosorb P AW or 1.5 g of glass beads: the salt was then reduced at 250° by passing the carrier gas for 1 h. At temperatures lower than 50° the materials in the injector tube were transferred to another unit (Fig. 1) that is cooled from 50 to -20° and the temperature is controlled thermostatically. It should be noted that glass beads are preferred over Chromosorb P AW as the catalyst support due to the low-temperature absorption of the latter.

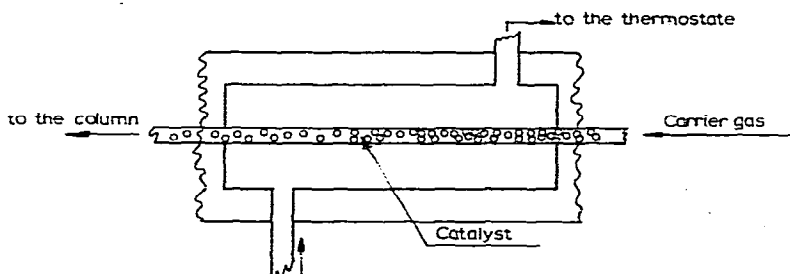


Fig. 1. Catalyst unit.

Sample injection system. The apparatus shown in Fig. 2 was used for introducing the sample into the gas chromatograph. The required amount of the sample is injected through the gas-sampling valve (D) into the carrier gas and with flow selection valves (H) the flow of carrier gas can be directed over the catalyst or bypassing it. When the sample is collected in a bottle and the gas-sampling loop cannot be used, the sample can be injected into the carrier gas through the injection port (F) using a gas-tight syringe. In order to avoid thermal exchange between the catalyst unit (I) and the injector port of the gas chromatograph (L), a Teflon (PTFE) tube (K) (1 in. \times 1/8 in.) was used as the connecting part.

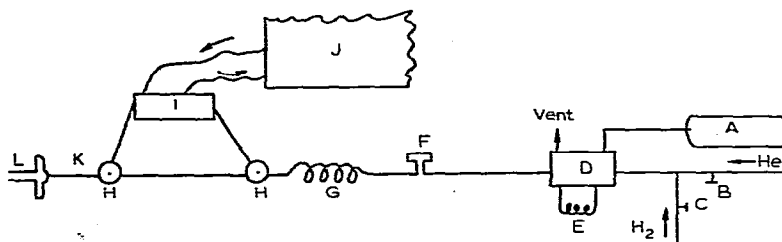


Fig. 2. Sample injection system. A = Sample tank; B = helium controller valve; C = hydrogen-flow controller valve; D = sampling valves; E = sampling loop (1 ml); F = syringe injection port; G = stainless-steel coil (1 ft. \times $\frac{1}{8}$ in.) in order to minimize the change of pressure at the column inlet when sample is injected through F; H = flow-selection valves; I = catalyst unit; J = constant-temperature refrigerating water-bath circulator; K = PTFE tube (1 in. \times $\frac{1}{8}$ in.); L = injector port of gas chromatograph.

Procedure

Preparation of vinyl chloride and ethyl chloride standards. To dilute vinyl chloride gas for a standard preparation (20 ppm), the exact volume of a bottle was determined (e.g., 1 l); the bottle was then fitted with an injection port and septum, equipped with a magnetic bar, purged with pure nitrogen gas and finally sealed with PTFE tape to prevent ingress of air. Vinyl chloride gas was taken from the original gas cylinder by means of a 5-ml syringe, and injected into the bottle through the septum. The contents of the bottle were mixed by use of the magnetic stirring bar for 5–10 min, or by moving the syringe plunger backwards and forwards about 20 times. This sample is denoted stock diluted VCM (5000 ppm). Another 1-l gas-dilution bottle was chosen, its volume determined and the inside purged as before. Knowing the gas concentration in the first bottle and the volume of the second bottle, any desired volume of the gas from the first bottle (in this case *ca.* 4 ml) can be removed with a gas-tight syringe and injected into the second bottle: The resulting sample is denoted the vinyl chloride standard (20 ppm).

The ethyl chloride standard in nitrogen was prepared by the same procedure, except that in this case the ethyl chloride samples are taken from a sealed 5-ml vial.

Sample collection from the working environment. An evacuated lecture bottle can be filled with air using a manual or a portable oil-free electrical pump until the inside pressure reaches 3 atm; several samples can be collected in the same manner from different areas and at different times. From these samples, the desired volume of gas (e.g., 1 ml) can be removed using a gas-tight syringe and then injected directly into the gas chromatograph through the sample-injection system (Fig. 2).

Method of testing. The standards and the samples can be injected either through the gas-sampling valve (D), or the injector-port septum (F), by choosing one of the flow-selection valves (H); these samples can either be passed over the catalyst and then analysed or can be analysed without passing over the catalyst (Fig. 2). By this method one can study the effect of the catalyst on pure, concentrated (4500 ppm) or diluted standard (20 ppm) samples of vinyl chloride at various temperatures. Attempts have also been made to find the best catalyst and the optimum hydrogenation conditions. The amount of vinyl chloride present in an unknown is determined by comparison of the chromatograms of the catalyzed and uncatalyzed sample with those of a standard; for this purpose, chromatograms are obtained of 1-ml injections

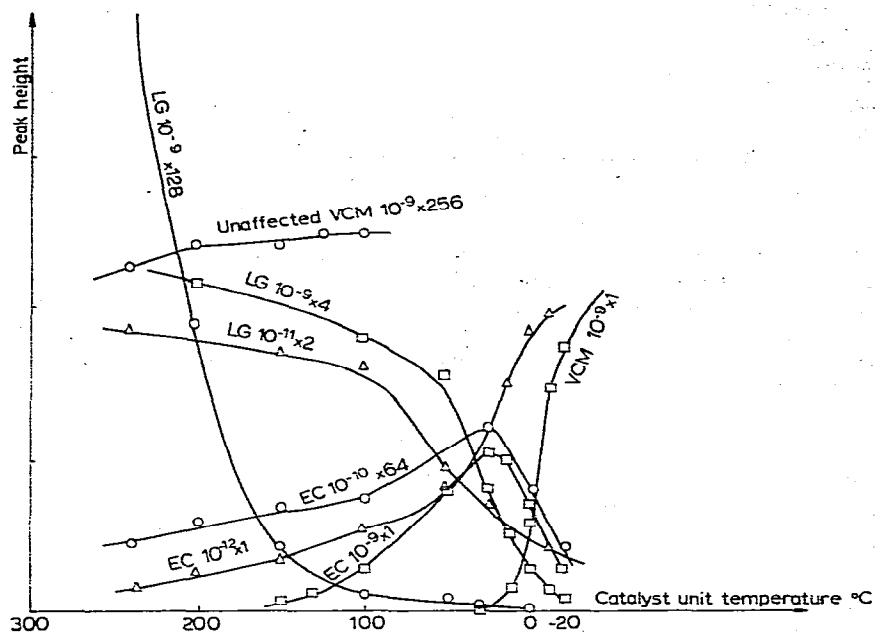


Fig. 3. Catalytic hydrogenation of vinyl chloride monomer (VCM) using 1.5 g of 0.1% Pd on glass beads (45-60 mesh). Curves: \circ , pure VCM; \square , 4500 ppm VCM in nitrogen (the line marked $\text{VCM } 10^{-9} \times 1$ represents unaffected VCM); \triangle , 20 ppm VCM in nitrogen. LG = light gas; EC = ethyl chloride. The numbers on the curves are electrometer settings.

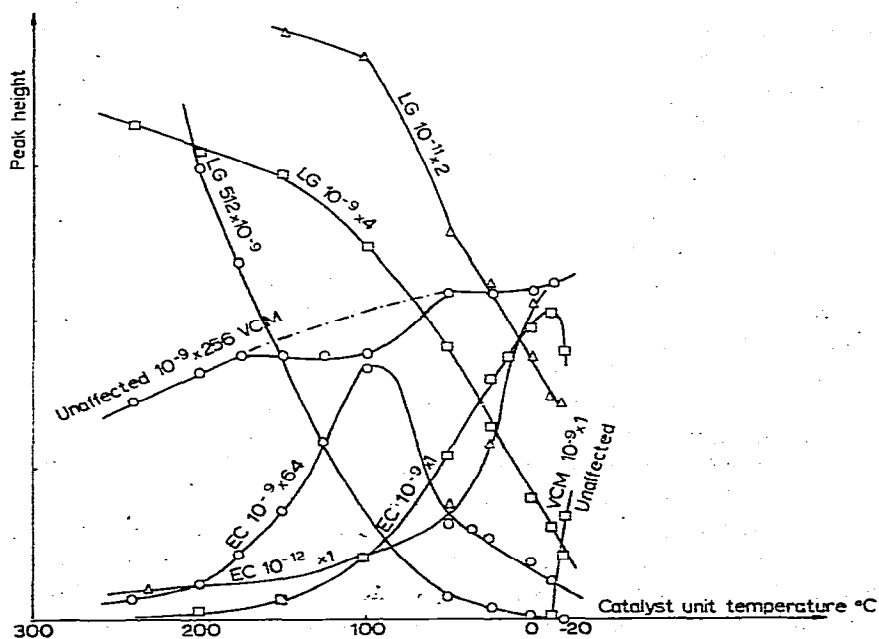


Fig. 4. Catalytic hydrogenation of vinyl chloride using 1.5 g of 1% Pd on glass beads (45-60 mesh). Details as in Fig. 3.

of (*e.g.* pure, concentrated or diluted) vinyl chloride passed over 1.5 g of 0.1 and 1% palladium on glass beads (45–60 mesh), and the peak heights for light gas, ethyl chloride and vinyl chloride were plotted *versus* temperature for each concentration (Figs. 3 and 4). In these diagrams the chromatographic data on each curve are the electrometer settings. A curve of the peak-height ratio of light gas to ethyl chloride *versus* temperature is shown in Fig. 5.

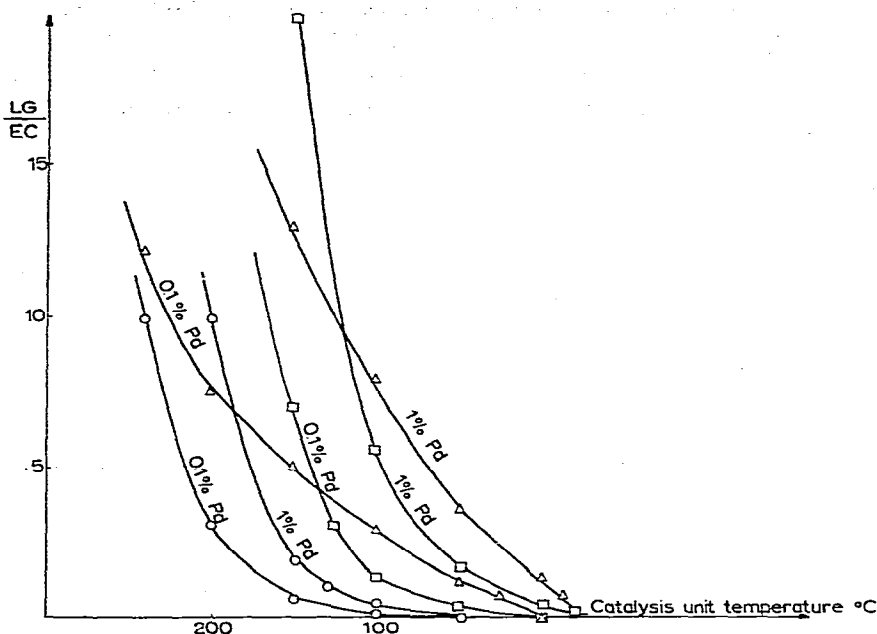


Fig. 5. Ratio of the peak heights of light gas and ethyl chloride produced on the catalytic hydrogenation of vinyl chloride. Details of curves as in Fig. 3.

RESULTS

Catalysis effect

Several metals such as Pt, Pd, Cu, Ni, W and Cr have been used. Of these, only Pt, Pd and Ni have a catalytic effect, and since the best results were obtained with Pd as a catalyst, this metal was used for the remainder of the study.

Temperature effect

In order to find the optimum temperature for the catalytic hydrogenation, we studied the process at various temperatures (*e.g.*, 250, 200, 150, 100, 50, 25, 0 and -20°) of the catalyst unit (Figs. 3–5). Referring to Fig. 3, on 0.1% Pd the amount of light gas decreases with decreasing temperature, and in the case of 4500 ppm of vinyl chloride the ethyl chloride curve reaches a maximum at 25° and the curve for unaffected vinyl chloride appears at 25° and has an increasing slope. In the case of pure vinyl chloride, at all the temperatures stated above there is some unaffected vinyl chloride and the ethyl chloride curve reaches a maximum at 30° . In the case of

20 ppm vinyl chloride, the ethyl chloride curve increases with decreasing temperature to -20° . Fig. 4 shows similar curves of light gas, ethyl chloride and unaffected vinyl chloride on 1% Pd.

Concentration effect

From Figs. 3 and 4 it can be seen that the catalytic hydrogenation of vinyl chloride is dependent on the concentration of the vinyl chloride and on the amount of the catalyst used; for instance, at 0° and 4500 ppm some of the vinyl chloride is not affected for a 0.1% Pd catalyst, while for 1% Pd all of the vinyl chloride is affected. The ratio of the light gas produced to that of ethyl chloride (LG/EC, Fig. 5) is also dependent on the concentration of vinyl chloride and percentage of metal in the catalyst.

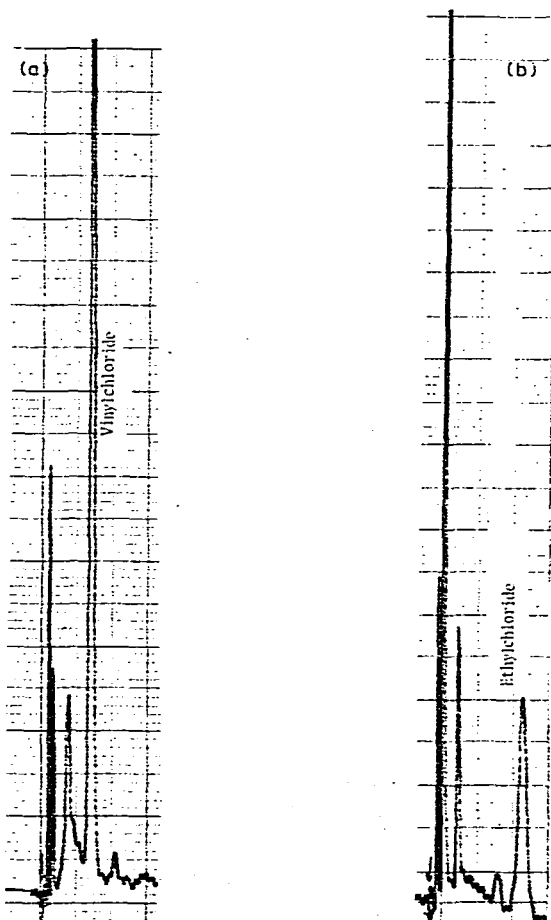


Fig. 6. Chromatograms of a sample of air containing vinyl chloride (50 ppm), before (a) and after (b) hydrogenation to ethyl chloride over 1% Pd on glass beads at 25° . Electrometer setting, 2×10^{-12} A/mV.

Other effects

The carrier gas flow-rate, amount of catalyst and volume injected are other factors which influence the catalytic hydrogenation, but these have been maintained constant in this study.

DISCUSSION

From these results, it can be concluded that of the catalysts chosen only palladium gives good results for vinyl chloride hydrogenation. During the hydrogenation process, some light gases are produced in addition to ethyl chloride. Since ethyl chloride is stable towards thermal decomposition up to 250°, it can be assumed that it is the vinyl chloride that decomposes to the light gases. The highest and optimum yield of ethyl chloride is dependent on the temperature and percentage of metal catalyst. For medium concentrations of vinyl chloride (e.g., 4500 ppm) the best results are obtained at 0° with 1% Pd, and for low concentrations of vinyl chloride (e.g., 20 ppm) the best results are achieved at -10° with 0.1% Pd. However, for a wide range of vinyl chloride concentrations (e.g., less than 5000 ppm), the former condition is preferred.

Fig. 6 shows chromatograms of a sample of air from a resin production factory, in which after the vinyl chloride peak can be identified from its shift on hydrogenation, and the amount of vinyl chloride can be calculated from the area of the ethyl chloride peak which is not affected by interfering peaks.

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REFERENCES

- 1 *Fed. Reg.*, 40, No. 171 (1975) 40529.
- 2 H. Huber, *Chem.-Ing.-Tech.*, 47 (1975) 803.
- 3 D. T. Williams and W. F. Miles, *J. Ass. Offic. Anal. Chem.*, 58 (1975) 272.
- 4 N. F. Ives, *J. Ass. Offic. Anal. Chem.*, 58 (1975) 457.
- 5 M. Beroza, *Anal. Chem.*, 34 (1962) 1801.