ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 5, pp. 663–666. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © A.A. Zirka, S.I. Reshetnikov, 2008, published in Kinetika i Kataliz, 2008, Vol. 49, No. 5, pp. 694–697.

Perchloroethylene Hydrofluorination in the Presence of a Chromium–Magnesium Catalyst

A. A. Zirka and S. I. Reshetnikov
Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Science, Novosibirsk, 630090 Russia
e-mail: reshet@catalysis.nsk.su

Received May 10, 2007

Abstract—The gas-phase hydrofluorination of perchloroethylene into pentafluoroethane (R-125) at $T = 330$–$390°C$ and $P = 0.4$ MPa in the presence of a chromium–magnesium catalyst is reported. The reaction rate under these conditions is described by a first-order equation. A hydrofluorination scheme including main product and by-product formation routes is deduced from the observed dependences of particular product selectivities on the total perchloroethylene conversion.

DOI: 10.1134/S0023158408050108

INTRODUCTION

Freons are used as foaming agents, propellants, extinguishants, gaseous sterilizing agents, and, most widely, refrigerants (both pure and mixed with other compounds) [1]. Under the Montreal Protocol On Substances That Deplete the Ozone Layer, the manufacture and consumption of ozone-depleting substances, such as chlorofluorocarbons, should be stopped within the next decade. This poses the challenging problem of gaining more detailed insight into the synthesis of next-generation, ethane-based Freons, such as pentafluoroethane (R-125). R-125 is obtained from perchloroethylene (PCE) in the presence of chromium-containing catalysts on various supports. In particular, chromium–magnesium catalysts are used for this purpose [2–7].

Here, we report the kinetics of PCE hydrofluorination into R-125 on a chromium–magnesium catalyst and discuss the reaction scheme taking into account formation of by-products.

EXPERIMENTAL

The catalyst was prepared by adding an aqueous solution of $CrCl_3$ to dry MgF_2 followed by mixing, pelletizing, and drying in air at 70–150°C. According to ICP spectrometric data, the resulting substance contained 12 wt % chromium chloride. The BET specific surface of the catalyst was 60 m^2/g. The dry catalyst (grain size of 0.25–0.50 mm) was treated with hydrogen fluoride in situ at 300–390°C.

PCE hydrofluorination experiments were carried out in a fixed-bed flow reactor. Liquid hydrogen fluoride, in a vessel placed on a balance, was forced out with nitrogen into a capillary heated to 120°C an oven. HF evaporated there and was directed to a saturator, in which it was saturated with PCE. Next, the mixture of the reactants was passed through a heated U-shaped nickel reactor charged with the catalyst. The mixture leaving the reactor was redirected to the oven, where, after being passed through a regulating valve, already at atmospheric pressure, it was introduced into absorbers filled with an alkali-metal carbonate. The unreacted HF and the resulting HCl were thus replaced with water and carbon dioxide. The gaseous reaction mixture downstream of the absorbers was sampled during the reaction to be analyzed on line by GLC. The reaction mixture leaving the absorbers was brought out of the oven and was condensed in a condenser. The condensate, which consisted of unreacted PCE and liquid products, including water, flowed down into a collector, and the remaining mixture of carbon dioxide and gaseous products was passed through a rotameter. The initial mixture fed into the reactor was also sampled during the experiment.

Reaction products were identified using a Varian chromatograph with a Saturn-2000 mass spectrometer.

The on-line chromatographic analysis conditions were as follows: 3 m × 3 mm stainless steel column packed with 20% PEHA on hydroxylated Silochrom C-120, oven temperature of 50°C (10 min), programmed heating to 150°C at a rate of 5°C, evaporator temperature of 200°C, thermal-conductivity detector temperature of 90°C, detector current of 150 mA, and carrier gas (helium) flow rate of 15 ml/min. The chromatograph was Tsvet 500M, and the sample volume was 0.5–1.5 cm^3 at 120°C.

From GLC data, we derived the mole fractions of PCE and the reaction products in the initial and reacted mixtures (upstream and downstream of the catalyst bed, respectively), as well as the total PCE conversion (X) as the ratio of the difference between the PCE mole fractions in the initial and reacted mixtures (corrected for the change in the mixture volume upon the reaction) to the PCE mole fraction in the initial mixture. Product

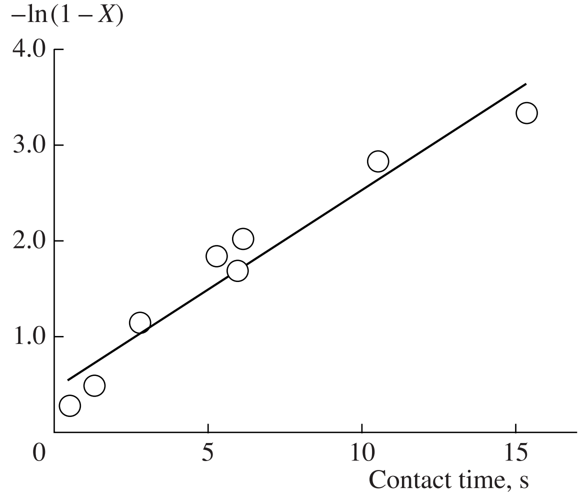


Fig. 1. $\ln(1-X)$ versus τ at 350°C.

selectivities (S_R, mol %) were calculated as the ratio of the mole fraction of a given product to the sum of the mole fractions of all products in the stream leaving the reactor.

The contact time (τ) was calculated for $T = 20°C$ and atmospheric pressure in the ideal gas approximation using the formula

$$\tau = [V/(24000A)][B/(1+B)],$$

where V is the volume of the catalyst (cm^3), A is the HF flow rate (mol/s), 24000 is the volume of 1 mol of an ideal gas at 20°C (cm^3), and B is the HF/PCE molar ratio.

All experiments were carried out in the kinetically controlled regime under conditions of stable catalyst operation.

RESULTS AND DISCUSSION

The dependence of the extent and rate of PCE hydrofluorination in the presence of the chromium–magnesium catalyst on the reaction conditions was investigated at the following process parameters: $T = 330$–$390°C$, pressure of 0.4 MPa, HF/PCE ratio of 50 : 1 to 6.6 : 1, and contact time of 0.3–16 s. The PCE conversion was 23–99%. Previous experiments demonstrated that, as the pressure is raised from 0.1 to 0.3 MPa, the reaction rate increases slightly. A further increase in the pressure obviously does not exert any appreciable effect on the reaction rate. The main reaction products under these conditions were fluorotrichloroethylene $CFCl{=}CCl_2$ (Freon R-1111), the difluorodichloroethylene isomers $CFCl{=}CFCl$ and $CF_2{=}CCl_2$ (R-1112 and R-1112a), difluorotrichloroethane CF_2Cl–$CHCl_2$ (R-122), the trifluorodichloroethane isomers $CHCl_2$–CF_3 and $CHFCl$–CF_2Cl (R-123 and R-123a), the tetrafluorochloroethane isomers CF_3–$CHFCl$ and CHF_2–CF_2Cl (R-124 and R-124a), and Freon R-125. The by-products were trifluorotrichloroethane CF_2Cl–$CFCl_2$ (Freon R-113), tetrafluorodichloroethane CF_2Cl–CF_2Cl (R-114), pentafluorochloroethane CF_3–CF_2Cl (R-115), trifluorochloroethane CH_2Cl–CF_3 (R-133a), and tetrafluoroethane CHF_2–CHF_2 (R-134).

At a constant temperature, pressure, and HF/PCE ratio, the PCE conversion increases with increasing contact time. The linear dependence of $-\ln(1-X)$ on τ (Fig. 1) possibly indicates that the reaction is first-order with respect to PCE. Monoparametrical experiments at a varied initial HF/PCE ratio showed that the mean reaction rate grows in proportion to the mean PCE concentration (Fig. 2) and that the order of the reaction with respect to PCE is close to unity. Thus, at a constant pressure in the presence of excess HF, the PCE hydrofluorination rate can be described by the equation

$$w = kC,$$

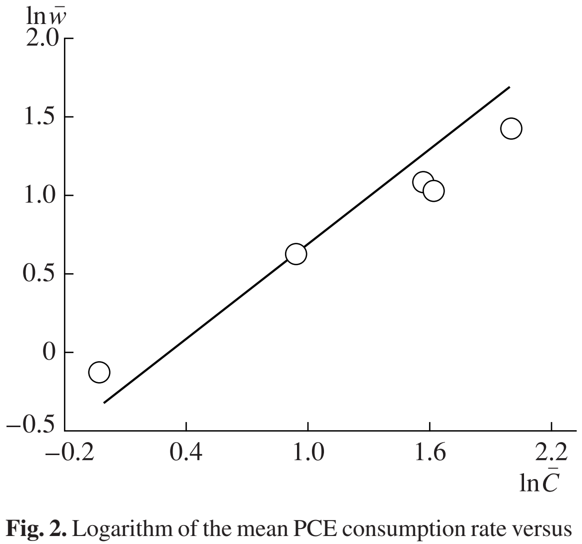


Fig. 2. Logarithm of the mean PCE consumption rate versus the logarithm of the mean PCE concentration.

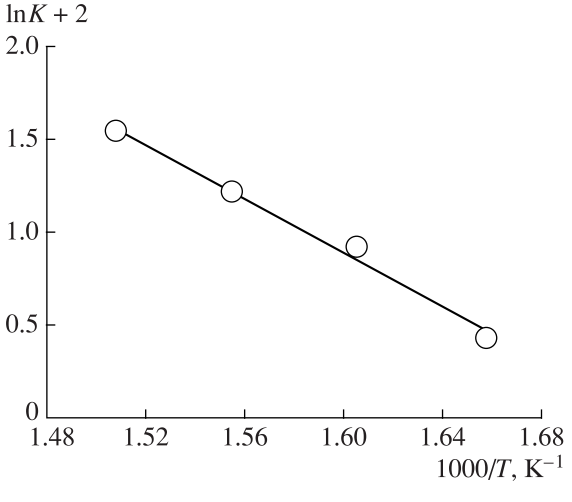


Fig. 3. Arrhenius plot of the rate constant of PCE hydrofluorination.

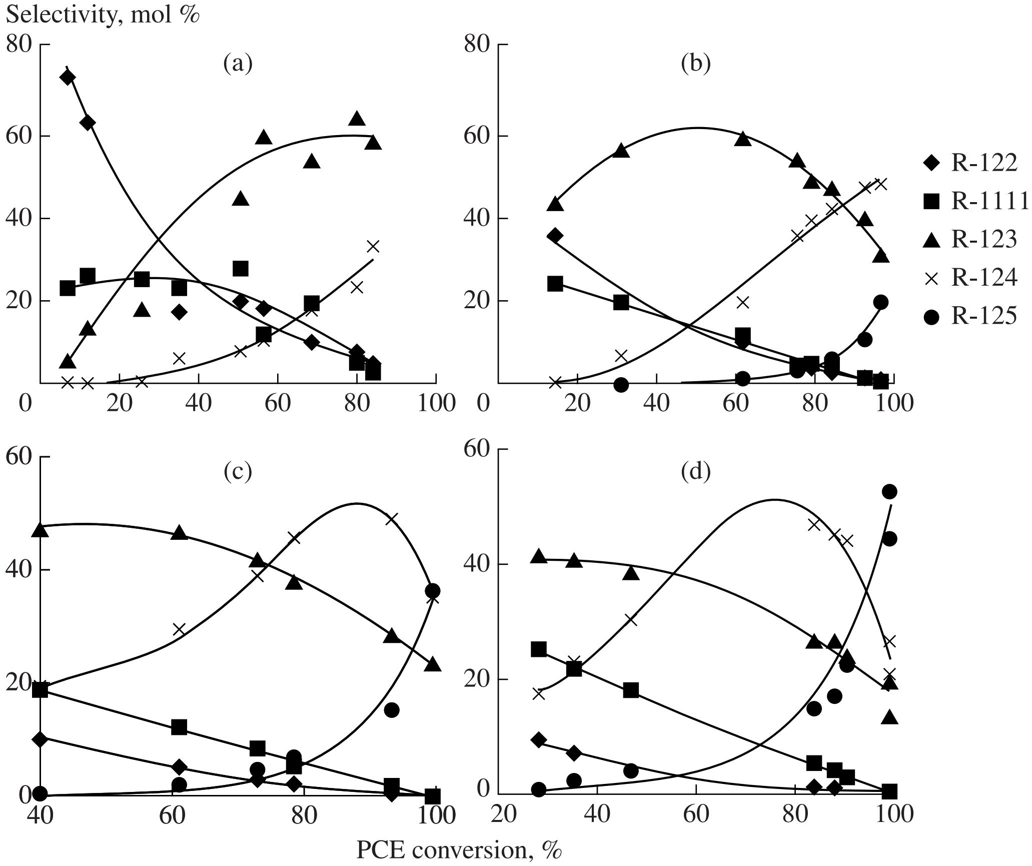


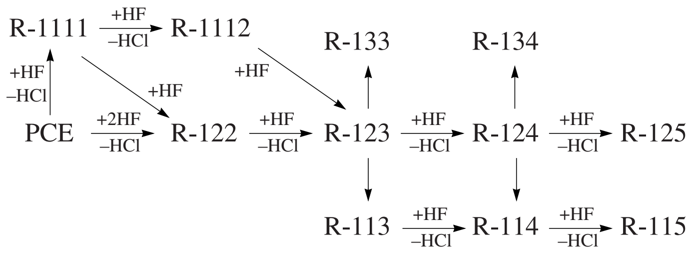
Fig. 4. Selectivities with respect to R-125 and its precursors as a function of the total PCE conversion at T = (a) 330, (b) 350, (c) 370, and (d) 390°C.

where C is the current PCE concentration in the stream and k is the first-order rate constant:

$$k = -\ln(1 - X)/\tau.$$

At a constant pressure, the reaction rate increases with increasing temperature. The logarithm of the rate constant depends linearly on the inverse temperature (Fig. 3). The apparent activation energy calculated from these data is 14.5 ± 1.7 kcal/mol, and the preexponential factor is $K_0 = 3.88 \times 10^4$ s^{-1}.

The product selectivities depend on the reaction temperature and total PCE conversion. For example, as the PCE conversion increases at a constant temperature, the selectivities $S_{\text{R-1111}}$ and $S_{\text{R-122}}$ decrease; $S_{\text{R-123}}$, $S_{\text{R-124}}$, and $S_{\text{R-114}}$ pass through a maximum; and $S_{\text{R-125}}$, $S_{\text{R-133}}$, and $S_{\text{R-115}}$ increase (Figs. 4, 5). The observed dependences are evidence that PCE hydrofluorination on the chromium–magnesium catalyst proceeds according to the following scheme:



According to this scheme, Freons R-1111, R-1112, R-122, R-123, and R-124 are precursors of Freon R-125, the main reaction product. The PCE consumption rate is determined by the rates of the following two parallel reactions:

(1) HF addition resulting in R-121, which quickly turns into R-122:

$$Cl_2C{=}CCl_2 + HF \longrightarrow HCl_2C\text{–}CCl_2F,$$

$$HCl_2C\text{–}CCl_2F + HF \longrightarrow HCl_2C\text{–}CClF_2;$$

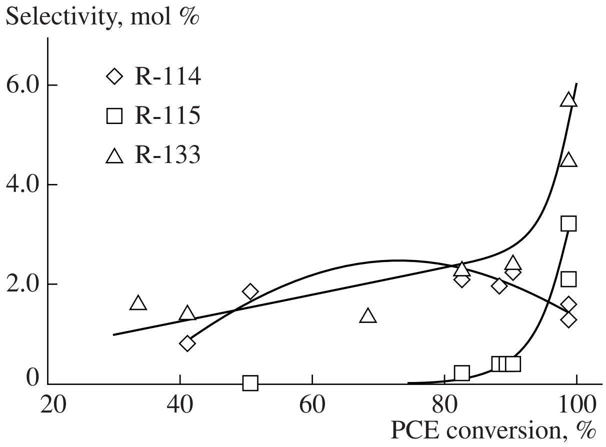


Fig. 5. By-product selectivities as a function of the total PCE conversion at 390°C.

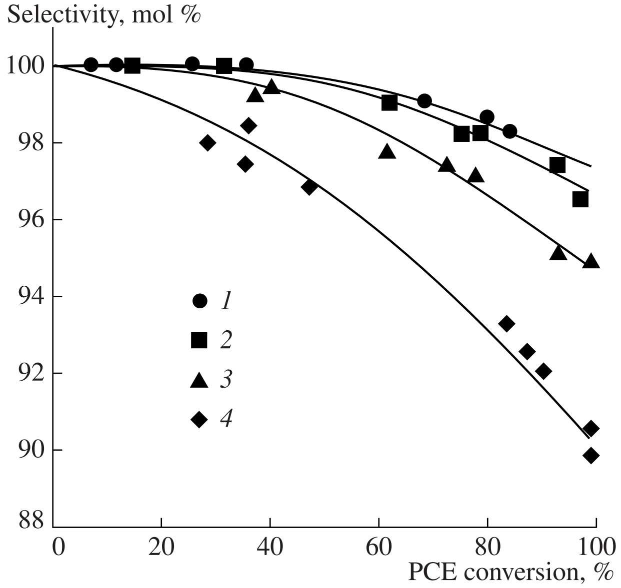


Fig. 6. Total product (R-125 + precursors) selectivity versus the total PCE conversion at T = (*1*) 330, (*2*) 350, (*3*) 370, and (*4*) 390°C.

(2) replacement of one chlorine atom by a fluorine atom in the PCE molecule, resulting in R-1111:

$$Cl_2C{=}CCl_2 + HF \longrightarrow Cl_2C = CClF + HCl.$$

It is likely that the first reaction dominates at low temperatures (Fig. 4a) and the second at higher temperatures (Fig. 4d).

The final products of the reaction are R-125, R-115, R-133, and R-134. The formation of the by-products R-113, R-133, R-114, and R-134 is due to the disproportionation of R-123 and R-124:

$$2C_2HCl_2F_3 \longrightarrow C_2H_2ClF_3 + C_2Cl_3F_3,$$

$$2C_2HClF_4 \longrightarrow C_2H_2F_4 + C_2Cl_2F_4.$$

The possibility of these reactions was reported earlier [1]. The resulting R-113 and R-114 turn into R-115 under the reaction conditions.

As the temperature is raised at a given PCE conversion, $S_{\text{R-125}}$ increases (Figs. 4b–4d) and the total product (R-125 + precursors) selectivity decreases (Fig. 6). The selectivity of the reaction with respect to the by-products, including R-115, increases with increasing temperature.

CONCLUSIONS

In the presence of the chromium–magnesium catalyst, the effect of the reaction conditions on the PCE hydrofluorination rate has been investigated at $T = 330$–390°C, $P = 0.4$ MPa, and an HF/PCE molar ratio of 50 : 1 to 6.6 : 1. The PCE consumption rate under these conditions is satisfactorily described by a first-order equation with respect to PCE. The apparent activation energy at $T = 330$–370°C is 14.5 ± 1.7 kcal/mol, and the preexponential factor is $k_0 = 3.88 \times 10^4$ s^{-1}. The selectivity of the reaction with respect to the useful reaction products (R-125 + precursors) decreases with an increasing total PCE conversion and increasing temperature. Conversely, the R-125 + by-products selectivity increases with increasing temperature and total PCE conversion. A reaction scheme including by-product formation routes has been derived from the observed dependences of the particular product selectivities on the total PCE conversion.

REFERENCES

1. Manzer, L.E. and Rao, V.N.M., in *Advances in Catalysis*, London: Academic, 1993, vol. 39, p. 329.
2. US Patent 5763701, 1998.
3. US Patent 5919728, 1999.
4. RF Patent 2141467, 1999.
5. US Patent 6165931, 2000.
6. RF Patent 2179885, 2002.
7. Zhul, Y., Fiedler, K., Rudiger, St., and Kemnitz, E., *J. Catal.*, 2004, vol. 219, p. 8.