

ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

A Study of Trichloroethylene Hydrofluorination
Using a Kinetic Model¹

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Abstract—The kinetic features of catalytic hydrofluorination of trichloroethylene and 2-chloro-1,1,1-trifluoroethane on chromium fluoride/magnesium fluoride catalyst were studied. The effect of pressure and addition of various components of the reaction mixture at the reactor inlet was studied using the developed model.

The procedure of production of 1,1,1,2-tetrafluoroethane by gas-phase catalytic hydrofluorination of trichloroethylene is well known in the world practice and is commercially used by various companies. There are many patents related to this procedure of tetrafluoroethane production [1–3] and to the catalyst production [4, 5]. In gas-phase fluorination processes, chromium(III) compounds in the form of fluorides and oxofluorides are mainly used.

At the same time, there are no published data on the kinetics and mechanism of hydrofluorination of trichloroethylene, which are necessary to design the reaction unit.

The goal of this work was to study experimentally this process on the chromium fluoride/magnesium fluoride catalyst and, based on the developed kinetic model, to study the effect of pressure and addition of various components of the reaction mixture (hydrogen chloride, 1,1-difluoroethylene, 1,1,1-trifluoroethane, and pentafluoroethane) at the reactor inlet.

EXPERIMENTAL

The study was carried out on a continuous installation consisting of a nickel reactor with electrical heating, units for dosing the initial reagents, and a system for collection and analysis of the synthesis products. The total capacity of the reactor was 1000 cm³; the inner diameter was 36 mm. The reactor temperature was monitored by a multizone thermocouple. Hydrogen fluoride and 2-chloro-1,1,1-trifluoroethane were

fed into the reactor through nickel capillaries. The flow rate of these reagents was set using the calibrating plot of the flow rate vs. the pressure in the service vessels, which, in turn, was produced by their temperature control. Trichloroethylene was fed into the reactor with a dosing pump. The flows of the initial reagents were mixed and fed into a coil-type evaporator equipped with electrical heating, and then into the reactor. After washing with water, neutralization, and drying, the reaction mixture was collected in a glass condenser cooled with a mixture of dry ice and CCl₄/CHCl₃.

The reaction mixture was analyzed on a Tsvet-500M chromatograph equipped with a heat conductivity detector. The 2-m chromatographic column was packed with ASK silica gel impregnated with liquid paraffin (10%).

The products were identified by gas chromatography–mass spectrometry on a Hewlett–Packard device equipped with an Al₂O₃/KCl capillary column (*l* = 50 m).

To determine the kinetic parameters, the experiments were performed in the reactor with a fluidized bed of the chromium fluoride/magnesium fluoride catalyst.²

The initial 2-chloro-1,1,1-trifluoroethane and trichloroethylene were purified by fractional distillation.

When developing the kinetic model, the following assumptions were made: the process is kinetically controlled; the catalyst activity is constant in time;

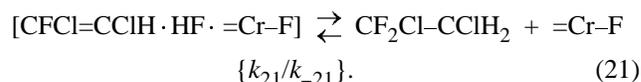
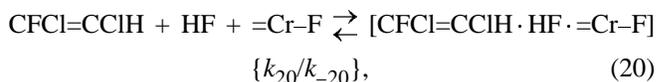
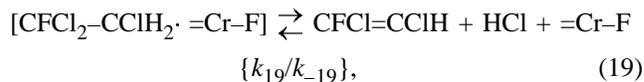
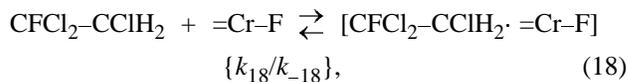
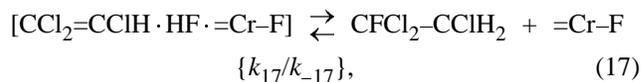
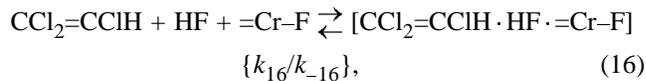
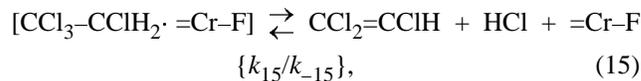
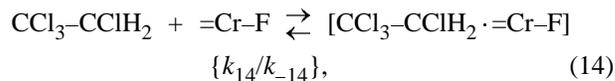
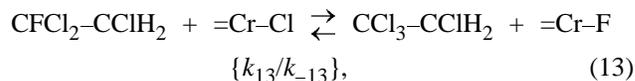
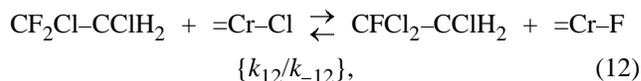
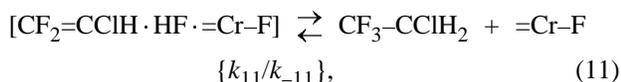
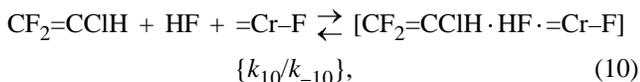
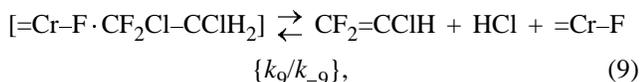
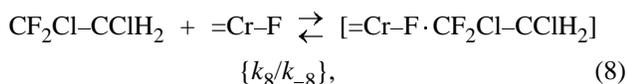
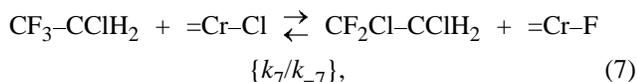
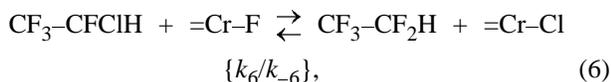
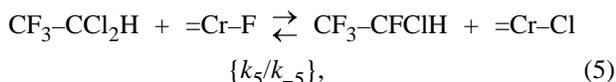
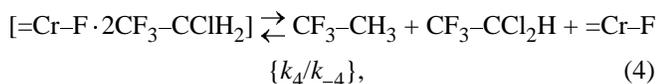
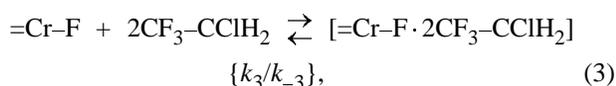
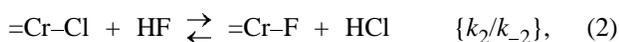
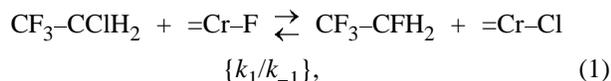
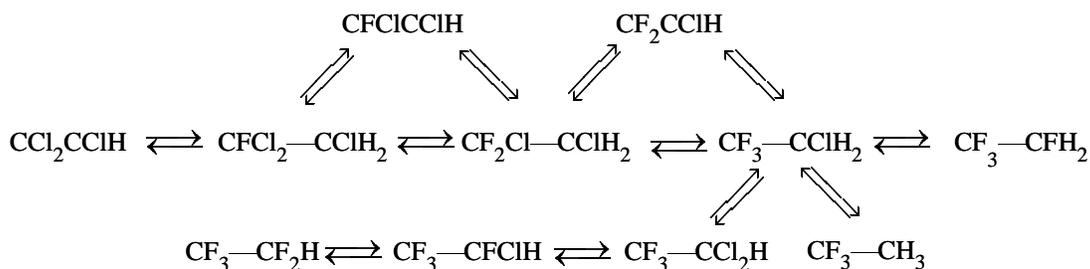
¹ Reported at the Third International Conference “Chemistry, Technology, and Application of Fluorine Compounds,” St. Petersburg, June 6–9, 2001.

² This catalyst (chromium fluoride applied to magnesium fluoride) is produced by the pilot plant of the Prikladnaya Khimiya Russian Scientific Center and is used in various hydrofluorination processes.

the catalyst can operate as a fluorine transfer agent; thermal decomposition of synthesis products is insignificant [6]; in the course of synthesis, products of asymmetric structure are mainly formed; only one fluorine atom in CrF_3 participates in exchange with chlorine atom; and the reaction of CrF_3 with HCl is significantly faster than the reaction of CrF_3 with

chlorine-containing organic compounds.

With these assumptions, the process scheme can be presented as a series of successive stages considering the processes related to production of 2-chloro-1,1,1-trifluoroethane from trichloroethylene and subsequent fluorination to 1,1,1,2-tetrafluoroethane:



Based on the developed scheme of this catalytic process, using the methods of pathways for com-

plicated reactions [7], we derived a kinetic model considering the stages of formation of 2-chloro-1,1,1-trifluoroethane and 1,1,1,2-tetrafluoroethane. In so doing, each reaction was considered as a multistage process [8]. The developed model describes variation of the concentrations of HF, HCl, CF₃-CClH₂, CF₃-CFH₂, CF₃-CH₃, CF₃-CCl₂H, CF₃-CFClH, CF₃-CF₂H, CF₂Cl-CClH₂, C₂HCl₃, CF₂=CClH, CFCI₂-CClH₂, and CFCl=CClH:

$$\frac{dc_1}{dt} = k'_{-7}c_8 - k_7c_1c_{11} - k'_1c_1 + k_{-1}c_3c_{11} + k'_{10}c_2c_{10} - k_{50}c_1 - 2k_3c_1^2 + 2k_n c_1^2 + 2k_t c_4c_{11},$$

$$\frac{dc_3}{dt} = k'_1c_1 - k_{-1}c_3c_{11},$$

$$\frac{dc_4}{dt} = k'_3c_1^2 - k_n c_1^2 - k_t c_4c_{11},$$

$$\frac{dc_5}{dt} = k'_3c_1^2 - k_n c_1^2 - k_t c_4c_{11} - k'_5c_5 + k_{-5}c_6c_{11},$$

$$\frac{dc_6}{dt} = k'_5c_5 - k_{-5}c_6c_{11} - k'_6c_6 + k_{-6}c_7c_{11},$$

$$\frac{dc_7}{dt} = k'_6c_6 - k_{-6}c_7c_{11},$$

$$\frac{dc_8}{dt} = k_{-12}c_2c_{12} - k_{12}c_8c_{11} - k'_{-7}c_8 + k_7c_1c_{11} - 0.5k'_8c_8 + 0.5k'_9c_{10}c_{11} + k'_{20}c_2c_{13},$$

$$\frac{dc_9}{dt} = -k'_{16}c_2c_9 + k_{\Sigma}c_8c_{11} + k_{\sigma}c_9c_{11},$$

$$\frac{dc_{10}}{dt} = 0.5k'_8c_8 - 0.5k'_{-9}c_{10}c_{11} - k'_{10}c_2c_{10} + k_{50}c_1,$$

$$\frac{dc_{12}}{dt} = k'_{16}c_2c_9 - k_{-12}c_2c_{12} + k_{12}c_8c_{11} - 0.5k'_{18}c_{12} + 0.5k'_{19}c_{11}c_{13},$$

$$\frac{dc_{13}}{dt} = 0.5k'_{18}c_{12} - 0.5k'_{19}c_{11}c_{13} - k'_{20}c_2c_{13},$$

$$c_2 = c_2^0 - 3(c_1 - c_1^0) - 4(c_3 - c_3^0) - 3(c_4 - c_4^0) - 3(c_5 - c_5^0) - 4(c_6 - c_6^0) - 5(c_7 - c_7^0) - 2(c_8 - c_8^0) - 2(c_{10} - c_{10}^0) - (c_{12} - c_{12}^0) - (c_{13} - c_{13}^0),$$

Table 1. Rate constants and activation energies of the process stages

| Rate constant | $\ln k_i$ | E , kcal mol ⁻¹ | Rate constant | $\ln k_i$ | E , kcal mol ⁻¹ |
|---------------|-----------|------------------------------|---------------|-----------|------------------------------|
| k_{Σ} | 43 | 50 | k_{σ} | →0 | |
| k'_1 | 11.7 | 18.3 | k_n | →0 | |
| k_{-1} | 15.6 | 12.2 | k_t | 8.5 | 5 |
| k'_5 | 30.5 | 33.7 | k'_3 | 26.2 | 35 |
| k_{-5} | 36.9 | 32.3 | k'_{-9} | 23.7 | 20 |
| k'_6 | 11 | 15 | k_{50} | 29.5 | 45 |
| k_{-6} | 22.7 | 20 | k'_{-12} | 82.8 | 77.6 |
| k_7 | 43.5 | 50 | k_{12} | 0.8 | 2.1 |
| k'_{-7} | 20.5 | 20 | k'_{18} | 38.7 | 34.9 |
| k'_8 | 17 | 20 | k'_{-19} | 58.7 | 49.6 |
| k'_{10} | 12.2 | 10 | k'_{20} | 46.7 | 38.8 |
| k'_{16} | 33.8 | 29.9 | | | |

$$c_{11} = c_{11}^0 + (c_1^0 - c_1) + 2(c_5^0 - c_5) + (c_6^0 - c_6) + 2(c_8^0 - c_8) + 3(c_9^0 - c_9) + (c_{10}^0 - c_{10}) + 3(c_{12}^0 - c_{12}) + 2(c_{13}^0 - c_{13}),$$

where c_1 is the concentration of CF₃-CClH₂ (Freon 133a), c_2 is that of HF, c_3 is that of CF₃-CFH₂ (Freon 134a), c_4 is that of CF₃-CH₃ (Freon 143a), c_5 is that of CF₃-CCl₂H (Freon 123a), c_6 is that of CF₃-CFClH (Freon 124a), c_7 is that of CF₃-CF₂H (Freon 125), c_8 is that of CF₂Cl-CClH₂ (Freon 132a), c_9 is that of C₂HCl₃ (trichloroethylene), c_{10} is that of CF₂=CClH (1,1-difluorochloroethylene), c_{11} is that of HCl, c_{12} is that of CFCI₂-CClH₂ (Freon 131), c_{13} is that of CFCl=CClH (1-fluoro-1,2-dichloroethylene); and k_i are the kinetic constants:

$$k_{\Sigma} = 2 \frac{k'_{14} k_{13} k_{12}}{k'_{-13} k_{-14}}, k_{\sigma} = \frac{k_{-14} k'_{14} k'_{-15}}{k_{-15} k'_{-13}}, k_n = \frac{k_{-3} k'_3}{k_{-3} + k_4},$$

$$k_t = \frac{k_{-3} k'_{-4}}{k_{-3} + k_4}, k_{50} = \frac{k_{-1} k'_{10}}{k'_{10} + k_{11}}$$

$$k'_i = k_i[\text{Cr-F}]; [\text{Cr-F}] \approx \text{const.}$$

The constants were determined by regression analysis. The functional to be minimized was the weighted sum of squared deviations of the experimental and calculated concentrations. As a procedure of numerical integration, we used the LSODA method designated for solving rigid systems of differential equations [9]. The functional was minimized by the Gauss-Newton method.

The kinetic constants obtained are listed in Table 1. The developed kinetic model is adequate in the

Table 2. Hydrofluorination of 2-chloro-1,1,1-trifluoroethane and trichloroethylene. Residence time 10 s

| Concentration at reactor inlet, M | | Concentration at reactor outlet, M |
|--|--|---|
| initial reactants | component added | |
| 2-Chloro-1,1,1-trifluoroethane* | | |
| $c_1^0 = 0.003733$, $c_2^0 = 0.01493$ | | $c_3 = 0.75 \times 10^{-3}$, $c_4 = 0.3 \times 10^{-4}$, $c_7 = 0.53 \times 10^{-5}$, $c_{10} = 0.75 \times 10^{-5}$ |
| $c_1^0 = 0.003733$, $c_2^0 = 0.01493$ | CF ₃ -CH ₃ : $c_4^0 = 0.3 \times 10^{-4}$ $c_4^0 = 0.6 \times 10^{-4}$ | $c_4 = 0.47 \times 10^{-4}$ $c_4 = 0.63 \times 10^{-4}$ |
| $c_1^0 = 0.003733$, $c_2^0 = 0.01493$ | CF ₃ -CF ₂ H: $c_7^0 = 0.53 \times 10^{-5}$ $c_7^0 = 1.6 \times 10^{-5}$ | $c_7 = 0.63 \times 10^{-5}$ $c_7 = 0.82 \times 10^{-5}$ |
| $c_1^0 = 0.003733$, $c_2^0 = 0.01493$ | CF ₂ = CClH: $c_{10}^0 = 0.1 \times 10^{-4}$ $c_{10}^0 = 0.8 \times 10^{-4}$ | $c_{10} = 0.75 \times 10^{-5}$ $c_{10} = 0.1 \times 10^{-4}$ |
| $c_1^0 = 0.003733$, $c_2^0 = 0.01493$ | HCl: $c_{11}^0 = 0.7 \times 10^{-5}$ $c_{11}^0 = 0.7 \times 10^{-4}$ $c_{11}^0 = 0.7 \times 10^{-3}$ | $c_{10} = 0.7 \times 10^{-5}$ $c_{10} = 0.7 \times 10^{-5}$ $c_{10} = 0.7 \times 10^{-5}$ $c_3 = 0.5 \times 10^{-3}$ |
| Trichloroethylene** | | |
| $c_2^0 = 0.01991$, $c_9^0 = 0.005856$ | | $c_4 = 0.35 \times 10^{-9}$, $c_7 = 0.45 \times 10^{-13}$, $c_{10} = 0.3 \times 10^{-4}$ |
| $c_2^0 = 0.01991$, $c_9^0 = 0.005856$ | CF ₃ -CH ₃ : $c_4^0 = 1 \times 10^{-5}$ | $c_4 = 0.45 \times 10^{-5}$ |
| $c_2^0 = 0.01991$, $c_9^0 = 0.005856$ | CF ₃ -CF ₂ H: $c_7^0 = 1 \times 10^{-5}$ | $c_7 = 0.87 \times 10^{-5}$ |
| $c_2^0 = 0.01991$, $c_9^0 = 0.005856$ | CF ₂ = CClH: $c_{10}^0 = 0.3 \times 10^{-4}$ | $c_{10} = 0.42 \times 10^{-4}$ |

* Molar ratio HF : CF₃-CClH₂ = 4 : 1, 380°C

** Molar ratio HF : C₂HCl₃ = 3.4 : 1, 200°C.

following intervals of the process parameters: temperature 175–420°C; molar ratio of reactants HF : C₂H₂ClF₃ = (2–18) : 1 and HF : C₂HCl₃ = (3.4–13.6) : 1.

Using this kinetic model, we studied the influence

α , γ , %; $c_1 \times 10^3$, $c_2 \times 10^7$, M

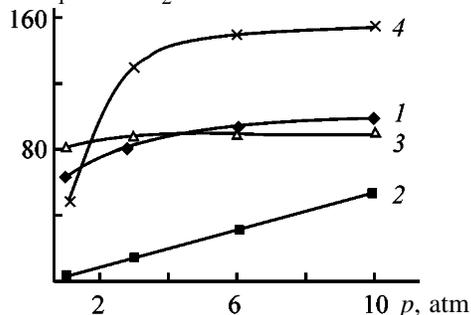


Fig. 1. Hydrofluorination of trichloroethylene: (1) conversion of trichloroethylene α , (2) concentration of 2-chloro-1,1,1-trifluoroethane $c_1 \times 10^3$, (3) selectivity with respect to 2-chloro-1,1,1-trifluoroethane γ , and (4) concentration of 1,1,1,2-tetrafluoroethane $c_2 \times 10^7$; (p) pressure.

of the process parameters on the main reaction stages. The influence of pressure was studied under the following conditions: molar ratio of reactants HF : C₂HCl₃ = 3.4 : 1, 200°C (first stage); HF : Freon 133a = 4 : 1, 380°C (second stage); and contact time $\tau = 10$ s. The course of the process was analyzed at a pressure of 1, 3, 6, and 10 atm. The results of evaluation (Figs. 1, 2) show the following.

(1) In the stage of trichloroethylene hydrofluorination with hydrogen fluoride to Freon 133a, conversion of trichloroethylene increases (to 95–97%) with increasing pressure to 6 atm, the selectivity with respect to Freon 133a increases up to a pressure of 3 atm and then becomes practically constant (approximately 90%); the concentration of Freon 134a increases up to a pressure of approximately 6 atm and then increases insignificantly, but the yield of by-products increases. Thus, increase of the pressure above 6 atm is not appropriate.

(2) In the stage of hydrofluorination of Freon 133a

Table 3. Hydrofluorination of 2-chloro-1,1,1-trifluoroethane*

| Run no. | Component added | Mixture composition, % | |
|---------|--|---|--|
| | | at reactor inlet (without HF) | at reactor outlet (without HF and HCl) |
| 1 | – | CF ₃ -CClH ₂ 97.02, others 2.98 | CF ₃ -CClH ₂ 71.45, CF ₃ -CFH ₂ 23.24, CF ₃ -CF ₂ H 2.38, CF ₃ -CH ₃ 1.86, others 1.08 |
| 2 | CF ₃ -CF ₂ H | CF ₃ -CClH ₂ 92.79, CF ₃ -CFH ₂ 0.46, CF ₃ -CF ₂ H 3.88, others 2.87 | CF ₃ -CClH ₂ 69.98, CF ₃ -CFH ₂ 22.29, CF ₃ -CF ₂ H 5.06, CF ₃ -CH ₃ 1.82, others 0.85 |
| 3 | CF ₃ -CF ₂ H | CF ₃ -CClH ₂ 85.79, CF ₃ -CFH ₂ 0.24, CF ₃ -CF ₂ H 12.43, CF ₃ -CH ₃ 0.04, others 1.5 | CF ₃ -CClH ₂ 64.89, CF ₃ -CFH ₂ 23.99, CF ₃ -CF ₂ H 7.82, CF ₃ -CH ₃ 2.11, others 1.19 |
| 4 | – | CF ₃ -CClH ₂ 99.69, CF ₃ -CH ₃ 0.12, others 0.19 | CF ₃ -CClH ₂ 62.96, CF ₃ -CH ₃ 3.56, CF ₃ -CFH ₂ 30.48, CF ₃ -CF ₂ H 2.08, others 0.92 |
| 5 | CF ₃ -CH ₃ | CF ₃ -CClH ₂ 99.0, CF ₃ -CH ₃ 0.68, others 0.32 | CF ₃ -CClH ₂ 64.23, CF ₃ -CH ₃ 3.58, CF ₃ -CFH ₂ 28.98, CF ₃ -CF ₂ H 2.44, others 0.77 |
| 6 | CF ₃ -CH ₃ | CF ₃ -CClH ₂ 92.49, CF ₃ -CH ₃ 7.14, others 0.37 | CF ₃ -CClH ₂ 60.58, CF ₃ -CH ₃ 8.48, CF ₃ -CFH ₂ 27.08, CF ₃ -CF ₂ H 2.73, others 1.13 |
| 7 | – | CF ₃ -CClH ₂ ~ 100 | CF ₃ -CClH ₂ 82.39, CF ₃ -CFH ₂ 16.93, CF ₂ =CClH 0.15, others 1.13 |
| 8 | Mixture of CF ₃ -CFH ₂ and CF ₂ =CClH | CF ₃ -CClH ₂ 71.45, CF ₃ -CFH ₂ 25.41, CF ₂ =CClH 1.56, others 1.58 | CF ₃ -CClH ₂ 56.66, CF ₃ -CFH ₂ 41.12, CF ₂ =CClH 0.10, others 2.12 |

* Reactor with fixed catalyst bed, $V=0.25$ l (run nos. 1–3) and with fluidized catalyst bed, $V=0.4$ l (run nos. 4–8); molar ratio HF : CF₃-CClH₂ = 8.3 : 1 (run nos. 1–3), 10 : 1 (run nos. 4–6), 19.6 : 1 (run nos. 7 and 8); temperature 400 (run nos. 1–3), 420 (run nos. 4–6), and 380°C (run nos. 7 and 8); residence time 4.8 (run nos. 1–3), 6.1 (run nos. 4–6), and 4.3 s (run nos. 7 and 8); with addition of a mixture of CF₃-CFH₂ and CF₂=CClH, 3 s).

with hydrogen fluoride, an increase in the pressure results in decreased conversion of Freon 133a; in this case, the conversion is decreased to the greatest extent in the pressure range from 1 to 3 atm (from 22.3 to 15.8%). At a higher pressure, the conversion becomes practically constant (14.6–14.9%). Thus, elevated pressure has a detrimental effect on this stage.

Calculated data on the effect of adding various components of the reaction mixture at the reactor inlet are listed in Table 2.

Our results show that addition of 2-chloro-1,1-difluoroethylene decreases the degree of its formation in the course of synthesis, i.e., in the process a mixture of Freon 134a and 2-chloro-1,1-difluoroethylene can be supplied to the reactor inlet for subsequent recovery. In a similar manner, addition of Freons 125 and 143a into the initial mixture decreases the degree of their formation in the course of synthesis. However, the presence of hydrogen chloride in the initial mixture in the stage of formation of Freon 134a from Freon 133a decreases the yield of Freon 134a. The results of the experiments confirmed the validity of evaluation of the influence of the process parameters (Table 3).

CONCLUSIONS

(1) Study of the process of 1,1,1,2-tetrafluoroethane production using the developed kinetic model describing the process in the temperature range 175–420°C at a molar ratio of reagents HF : C₂H₂ClF₃ = (2–18) : 1, HF : C₂HCl₃ = (3.4–13.6) : 1 showed that an increase in pressure to 6 atm has a positive effect on the conversion and selectivity in hydrofluorination

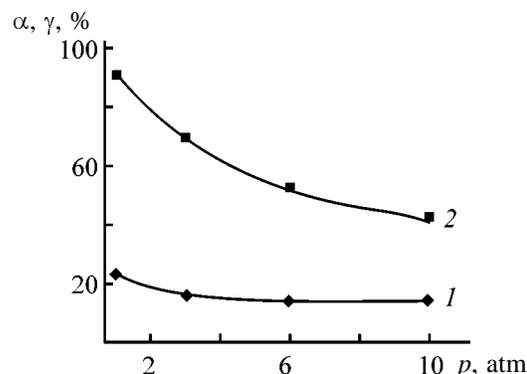


Fig. 2. Hydrofluorination of 2-chloro-1,1,1-trifluoroethane: (1) conversion of 2-chloro-1,1,1-trifluoroethane α and (2) selectivity with respect to 1,1,1,2-tetrafluoroethane γ ; (p) pressure.

of trichloroethylene. However, in hydrofluorination of 2-chloro-1,1,1-trifluoroethane, an increase in pressure to 3 atm adversely affects the process.

(2) A partial return of by-products (pentafluoroethane, 1,1,1-trifluoroethane, and 2-chloro-1,1-difluoroethylene) to synthesis decreases their formation in the synthesis.

(3) Owing to reversibility of 2-chloro-1,1,1-trifluoroethane hydrofluorination, the presence of hydrogen chloride in the initial reaction mixture adversely affects the process of 1,1,1,2-tetrafluoroethane production. Removal of hydrogen chloride from the reaction area is favorable for increasing the yield of the target product.

REFERENECES

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