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Non-ozone-depleting hydrofluorocarbons

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The state-of-the-art of transition of the chemical sector producing ozone-depleting substances (ODS) in Russia to non-ozone-depleting substances (NODS) is considered. The review summarizes the studies conducted by the Russian Scientific Center "Applied Chemistry" (St.Petersburg) and a number of Russian Academy Institutes including substantiation for the production methods of non-ozone-depleting hydrofluorocarbons; the most probable chemical mechanisms of their synthesis; the basis for standard process flow diagrams to be used in their full-scale manufacture; and the information on actual and newly created NODS production facilities in the Russian Federation.

Key words: hydrofluorocarbons, difluoromethane, 1,1-difluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoroethane, pentafluoroethane, gas-phase fluorination, liquid-phase fluorination.

Chlorofluorocarbons and bromofluorocarbons (chladones and halons), which possess a number of unique properties, in particular, chemical intertness, lack of toxicity, and explosion and fire safety, have been widely used in engineering as aerosol propellants, refrigerating fluids, foaming agents for plastics, solvents, highly efficient extinguishing agents, *etc*. However, the destructive impact of some chlorine- and bromine-containing compounds on the ozone layer discovered in the 1980s has attracted attention to the large group of industrial chladones containing chlorine or bromine as potentially hazardous compounds. Recent estimates of the relative roles of anthropogenic and natural factors on ozone layer depletion have shown that ~50% of the observed reduction of the ozone content above the Moscow Region are related to man´s impact, while the other are due to natural reasons. The contribution of anthropogenic factors above the Western Europe is ~75%; that above the US East Coast is 60%; and those above Japan, Baikal, and the Far East are 50%. In view of the fact that only the man-made component of the overall flow of ozone-depleting substances (ODS) that enters the atmosphere can be efficiently controlled, the international measures on the control of production and consumption of these substances appear to be a reasonable step toward sustainable development of the mankind.

The Vienna Convention for the Protection of the Ozone Layer adopted in 1985 was the first international document to stipulate measures for protection of the ozone layer. The states that signed the Convention undertook to cooperate in the control and prevention of the activity potentially threatening the stratosphere ozone layer. In September 1987, the Montreal Protocol (MP) on Substances That Deplete The Ozone Layer was adopted. Since the destructive role of chlorine and bromine has been confirmed by many research groups by that time, the Appendix to the MP listed the ODS subject to control by all countries involved in the MP. The list included chlorofluorocarbons (CFC), bromofluorocarbons (halons), and some chlorohydrocarbons. The Montreal Protocol applied obligations on the parties to restrict the consumption, production, and import/export of the ODS.

The Soviet Union was a first-rate world manufacturer of ODS: in 1987, it accounted for ~15% of the world output of these chemicals (~200 mt/y). Simultaneously, USSR was a first-rate consumer and a heavy exporter of ODS, who supplied these products not only to all of its union republics but also to a number of European and Asian countries. Ozone-depleting substances were manufactured at six large chemical plants of the Russian Federation. Chladones were consumed by almost every branch of industry in the Russian Federation.[1,2] In 1990, the structure of chladone application was as follows: the manufacture, repair, and maintenance of the domestic, commercial, and industrial refrigerating equipment, 27%; production of aerosol-packaged goods, 45%; manufacture of foamed materials, 11%; the use of chladones as sol-

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vents, 14%; production of fire-extinguishing means, 2%; other, 1%.

As the legal successor of the USSR, which ratified the Montreal Protocol on Substances That Deplete The Ozone Layer in 1988, the Russian Federation has fully accepted and undertook the obligation to stop the manufacture and consumption of the ODS, as stipulated by this international agreement. After the MP had been confirmed, the measures on the control of the manufacture and consumption of the ODS were given the state significance.

A large body of work for switching the industry to a new class of substances instead of the forbidden ODS was accomplished by the Russian Scientific Center "Applied Chemistry" in cooperation with some other Russian institutes. As a result of this research, a range of new chladones has been proposed, in particular, hydrofluorocarbons 134a (CF_2CFH_2), 152a (CF_2HCH_3), 125 (CF_3CF_2H), 32 (CH_2F_2), *etc*. The key distinction of the non-ozone-depleting substances from ODS is that they contain no chlorine or bromine atoms, which could be involved in the "chlorine" or "bromine" cycles of ozone decomposition. In addition to a zero ozone-depleting potential (ODP) and an admissible global warming potential (GWP), the main criterion applied to the choice of ODS substitutes is the proximity of the physicochemical and service properties to the corresponding properties of the ODS being replaced. The compliance with this criterion ensures the most facile transition of the industry to non-ozone-depleting substitutes of ODS.[2] The main range of non-ozone-depleting compounds accepted for the development and implementation to industry in the Russian Federation is presented in Table 1.

The production processes of non-ozone-depleting hydrofluorocarbons were mainly based on two methods of synthesis, depending on the compound structure and taking into account the available production facilities for the manufacture of chladone 11, 12, and 113, in particular, (i) liquid-phase fluorination of organochlorine compounds with anhydrous hydrogen fluoride (chladones 152a, 32, 143a, and so on) and (ii) gas-phase catalytic fluorination of organochlorine compounds with anhydrous hydrogen fluoride (chladones 134a, 125, and so on).

The main feedstock for the manufacture of non-ozone-depleting chladones (trichloroethylene, perchloroethylene, vinylidene chloride, vinyl chloride, and chloromethanes) is produced at some plants in Russia, namely the open joint-stock companies Kaustik (Volgograd), Khimprom (Volgograd), Kaustik (Sterlitamak), Usol´ekhimprom (Usol´e Sibirskoe), Sayanskkhimprom (Sayansk), and Khimprom (Cheboksary). Hydrogen fluoride is produced at chemical industry plants, namely, the open joint-stock company Galogen (Perm´), the open joint-stock company "B. P. Konstantinov Kirovo-Chepetsk Chemical Integrated Plant" (Kirovo-Chepetsk), and the Federal State Unitary Enterprises "Siberian Chemical Integrated Plant" (Tomsk) and "Angarsk Electrochemical Integrated Plant" (Angarsk).

Table 1. Hydrofluorocarbons approved for development and industrial implementation in the Russian Federation and their most

Parameter	Chladone 23	Chladone 32	Chladone 125	Chladone 134	Chladone 134a
Formula	CHF_3	CH_2F_2	C_2F_5H	CHF_2CHF_2	CH_2FCF_3
Molecular weight	70.1	52.024	120.022	102.03	102.03
B.p./°C 0.1 MPa	−82.2	−51.7	−48.5	−22.5	−26.5
Freezing point/°C	−155.15	−136	−103	−89.0	−101
Critical temperature/°C	25.85	78.4	67.7	110.25	101.5
Critical pressure/ MPa	4.82	5.843	3.39	3.77	4.06
Concentration limits of flame propagation in air (% v/v)	No	14.2—30.0	No	No	No
Self-ignition point/°C	765	504	—	630	—
Ozone-depleting potential (ODP) relative to CFH 11	0	0	0	0	0
Global warming potential (GWP) relative to CO_2	14800	880	3800	1200	1600
Toxicity: permissible exposure limit (DuPont) /ppm (v/v)	1000	1000	—	1000	—
MPC (work area) /mg m^{-3}	3000	3000	1000	—	3000
Hazard class	4	4	4	—	4

Let us consider characteristic features of the liquid-phase catalytic hydrofluorination taking the synthesis of difluoromethane (chladone 32) as an example.[4]

The synthesis occurs according to Scheme 1.

Scheme 1

$$\mathrm{SbCl_5 + HF \xrightarrow{k_0} SbCl_nF_{5-n} + HCl}$$

$$\mathrm{CH_2Cl_2 + SbCl_nF_{5-n} \xrightarrow[HF]{k_1} CH_2ClF + SbCl_{n+1}F_{4-n} + HCl}$$

$$\mathrm{CH_2ClF + SbCl_nF_{5-n} \xrightarrow[HF]{k_2} CH_2F_2 + SbCl_{n+1}F_{4-n} + HCl}$$

The kinetics of dichloromethane fluorination is described by the following equations:[5]

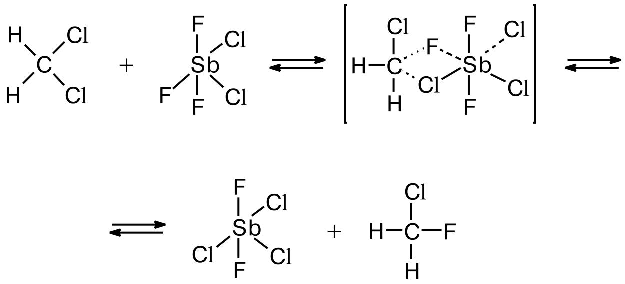
$$-r_{\mathrm{CH_2Cl_2}} = 2.2 \cdot 10^5/\{\exp(-5.8 \cdot 10^7/RT) \cdot C_{\mathrm{CH_2Cl_2}} \cdot C_{\mathrm{k}}\},$$

$$r_{\mathrm{CH_2F_2}} = 8.3 \cdot 10^5/\{\exp(-6.2 \cdot 10^7/RT) \cdot C_{\mathrm{CH_2ClF}} \cdot C_{\mathrm{k}}\},$$

where $C_{\mathrm{CH_2Cl_2}}$, $C_{\mathrm{CH_2ClF}}$, and C_{k} are the concentrations of dichloromethane, chlorofluoromethane, and the catalyst, respectively.

The composition of the catalyst used for the synthesis of chladone 32 was determined to be $(SbF_3)_{0.3} \cdot (SbCl_2F_3)_{0.7}$. The formation mechanism of fluoroalkanes and the role of antimony compounds are based on the ability of $SbCl_nF_{5-n}$ to form complexes with chloroalkanes (Scheme 2), which is followed by intramolecular exchange of fluorine atoms by chlorine.

Scheme 2



The kinetic data were used to calculate a 1000-ton-per-year reactor for the synthesis of chladone 32. The synthesis is carried out at a temperature of 95—105 °C and a pressure of 1.5—2.0 MPa. A process flow diagram for the synthesis of chladone 32 has been developed. This scheme is typical of the liquid-phase synthesis of non-ozone-depleting chladones. The same process flow diagram is applied to produce chladone 152a from vinyl chloride and hydrogen fluoride at 90 °C and 0.6—0.8 MPa in the presence of tin tetrachloride as the catalyst[6] and to produce chladone 245fa from pentachloropropane and

important properties[3]

Chladone 143a	Chladone 152a	Chladone 227ea	Chladone 236fa	Chladone C336	Chladone C438	Chladone 43—10mee
CF_3CH_3	CH_3CHF_2	CF_3CFHCF_3	$CF_3CH_2CF_3$	$C_4F_6H_2$-*cyclo*	$C_5F_8H_2$-*cyclo* $CHFCF_2CF_3$	CF_3CHF
84.041	66.05	170.03	152.039	164	214	252.053
−47.6	−24.55	−18.3	−0.7 (−1.4)	63	79	47.0
−111.3	−117.0	−131.2	−93.6	—	—	−80
73.1	113.5	103.5	130.7	—	—	—
4.11	4.491	2.95	3.18	—	—	—
9.2—18.4	3.9—16.9	No	No	—	—	—
720	453	>650	—	—	—	—
0	0	0	0	—	—	0
5400	190	3800	9400	—	—	1700
—	1000	—	—	—	—	—
3000	3000	—	—	—	—	—
4	4	—	—	—	—	—

hydrogen fluoride in the presence of $SbCl_5$ at a temperature of 100—120 °C and a pressure of 1.6—1.8 MPa.[7]

However, the liquid-phase hydrofluorination procedure has a number of limitations.

1. Replacement of chlorine by fluorine in the $—CH_2Cl$ and $=CHCl$ groups proceeds with great difficulty.

2. During hydrofluorination, the $SbCl_nF_{5-n}$ catalyst can function as a chlorinating agent giving rise to ozone-depleting chlorofluoroalkanes.

Therefore, hydrofluorocarbons with high fluorine contents (CF_3CFH_2, CF_3CF_2H) are prepared by gas-phase catalytic hydrofluorination.

Characteristic features of gas-phase catalytic hydrofluorination will be considered in relation to the synthesis of 1,1,1,2-tetrafluoroethane (chladone 134a) from trichloroethylene and hydrogen fluoride. The process occurs in two stages (Scheme 3).

Scheme 3

$$C_2HCl_3 + 3\,HF \longrightarrow C_2H_2ClF_3 + 2\,HCl + 93\ kJ\ mol^{-1} \qquad (1)$$

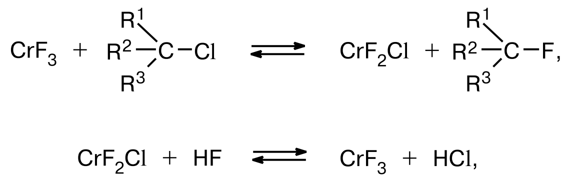
$$C_2H_2ClF_3 + HF \longrightarrow C_2H_2F_4 + HCl - 18\ kJ\ mol^{-1} \qquad (2)$$

As follows from the experimental data and thermodynamic calculations for stage (1), the chladone 133a content in the organic fraction of the synthesis products can reach 90—98%.

Stage (2) is reversible. Depending on the conditions, the content of chladone 134a in the organic fraction of the products may amount to 10—40% v/v. This process is carried out with a chromium magnesium fluoride catalyst[8,21] produced by impregnating a magnesium fluoride powder with a solution of chromium chloride followed by mixing, molding, drying, and treatment with hydrogen fluoride to convert $CrCl_3$ into the fluoride CrF_3.[9,10]

Study of the mechanism of catalyst action in this reaction has shown that the catalyst role is to transport fluorine and chlorine atoms.[11—13] The hydrofluorination of chlorofluoroethanes can be represented as Scheme 4

Scheme 4



$$CrF_3 + R^1R^2R^3C{-}Cl \rightleftharpoons CrF_2Cl + R^1R^2R^3C{-}F,$$

$$CrF_2Cl + HF \rightleftharpoons CrF_3 + HCl,$$

where chlorine in fluorochloroethane is replaced by fluorine on treatment with chromium fluoride whose composition thus changes to CrF_2Cl; subsequently, chlorine in the active part of the catalyst is replaced by fluorine under the action of hydrogen fluoride, which gives hydrogen chloride and CrF_3. This mechanism seems more likely than the mechanism[14,15] that includes the reaction between the HF molecules and chloroalkane adsorbed on neighboring active sites of the catalyst.

Together with the major hydrofluorination processes, dehydrofluorination, dehydrochlorination, and disproportionation reactions also take place in the presence of this catalyst (Scheme 5).

Scheme 5

$$CF_3{—}CH_2Cl \rightleftharpoons CF_2{=}CHCl + HF$$

$$CFCl_2{—}CH_2Cl \rightleftharpoons CFCl{=}CHCl + HCl$$

$$2\,CF_3{—}CH_2Cl \rightleftharpoons CF_3{—}CH_2F + CHF_2{—}CHCl_2$$

The resulting unsaturated fluorine-containing compounds (especially $CF_2{=}CHCl$, which forms an azeotrope with 1,1,1,2-tetrafluoroethane) complicate the subsequent isolation of the target product from the reaction mixture. The mechanism of these process involves the formation of active intermediate complexes on the catalyst surface.

Generally, taking into account the above assumptions, hydrofluorination of trichloroethylene can be represented by the following sequence of steps (Scheme 6).

Scheme 6

$$CCl_2{=}CClH + HF + CrF_3 \rightleftharpoons [CCl_2{=}CClH \cdot HF \cdot CrF_3] \qquad (1)$$

$$[CCl_2{=}CClH \cdot HF \cdot CrF_3] \rightleftharpoons CFCl_2{—}CClH_2 + CrF_3 \qquad (2)$$

$$CFCl_2{—}CClH_2 + CrF_3 \rightleftharpoons [CFCl_2{—}CClH_2 \cdot CrF_3] \qquad (3)$$

$$[CFCl_2{—}CClH_2 \cdot CrF_3] \rightleftharpoons CFCl{=}CClH + HCl + CrF_3 \qquad (4)$$

$$CFCl{=}CClH + HF + CrF_3 \rightleftharpoons [CFCl{=}CClH \cdot HF \cdot CrF_3] \qquad (5)$$

$$[CFCl{=}CClH \cdot HF \cdot CrF_3] \rightleftharpoons CF_2Cl{—}CClH_2 + CrF_3 \qquad (6)$$

$$CFCl_2{—}CClH_2 + CrF_3 \rightleftharpoons CF_2Cl{—}CClH_2 + CrF_2Cl \qquad (7)$$

$$HF + CrF_2Cl \rightleftharpoons HCl + CrF_3 \qquad (8)$$

$$CFCl_2{—}CClH_2 + CrF_2Cl \rightleftharpoons CCl_3{—}CClH_2 + CrF_3 \qquad (9)$$

$$CCl_3{—}CClH_2 + CrF_3 \rightleftharpoons [CCl_3{—}CClH_2 \cdot CrF_3] \qquad (10)$$

$$[\mathrm{CCl_3{-}CClH_2 \cdot CrF_3}] \rightleftharpoons \mathrm{CCl_2{=}CClH + HCl + CrF_3} \quad (11)$$

$$\mathrm{CF_2Cl{-}CClH_2 + CrF_3} \rightleftharpoons [\mathrm{CF_2Cl{-}CClH_2 \cdot CrF_3}] \quad (12)$$

$$[\mathrm{CF_2Cl{-}CClH_2 \cdot CrF_3}] \rightleftharpoons \mathrm{CF_2{=}CClH + HCl + CrF_3} \quad (13)$$

$$\mathrm{CF_2{=}CClH + HF + CrF_3} \rightleftharpoons [\mathrm{CF_2{=}CClH \cdot HF \cdot CrF_3}] \quad (14)$$

$$[\mathrm{CF_2{=}CClH \cdot HF \cdot CrF_3}] \rightleftharpoons \mathrm{CF_3{-}CClH_2 + CrF_3} \quad (15)$$

$$\mathrm{CF_2Cl{-}CClH_2 + CrF_3} \rightleftharpoons \mathrm{CF_3{-}CClH_2 + CrF_2Cl} \quad (16)$$

$$\mathrm{CF_3{-}CClH_2 + CrF_3} \rightleftharpoons \mathrm{CF_3{-}CFH_2 + CrF_2Cl} \quad (17)$$

$$\mathrm{2\,CF_3{-}CClH_2 + CrF_3} \rightleftharpoons [\mathrm{2\,CF_3{-}CClH_2 \cdot CrF_3}] \quad (18)$$

$$[\mathrm{2\,CF_3{-}CClH_2 \cdot CrF_3}] \rightleftharpoons \mathrm{CF_3{-}CH_3 + CF_3{-}CCl_2H + CrF_3} \quad (19)$$

On the basis of the proposed mechanism and using the pathway method for complex reactions,[16] a kinetic model for the synthesis of 1,1,1,2-tetrafluoroethane has been developed[17]

$$\mathrm{d}c_1/\mathrm{d}\tau = k'_{16}c_8 - k_{-16}c_1c_{11} - k'_{17}c_1 + k_{-17}c_3c_{11} + k'_{14}c_2c_{10} - k_\mathrm{B}c_1 - 2\,k'_{18}c_1^{\,2} + 2\,k_Dc_1^{\,2} + 2\,k_Cc_4c_{11}$$

$$\mathrm{d}c_3/\mathrm{d}\tau = k'_{17}c_1 - k_{-17}c_3c_{11}$$

$$\mathrm{d}c_4/\mathrm{d}\tau = k'_{18}c_1^{\,2} - k_Dc_1^{\,2} - k_Cc_4c_{11}$$

$$\mathrm{d}c_5/\mathrm{d}\tau = k'_{18}c_1^{\,2} - k_Dc_1^{\,2} - k_Cc_4c_{11} - k'_{20}c_5 + k_{-20}c_6c_{11}$$

$$\mathrm{d}c_6/\mathrm{d}\tau = k'_{20}c_5 - k_{-20}c_6c_{11} - k'_{21}c_6 + k_{-21}c_7c_{11}$$

$$\mathrm{d}c_7/\mathrm{d}\tau = k'_{21}c_6 - k_{-21}c_7c_{11}$$

$$\mathrm{d}c_8/\mathrm{d}\tau = k'_7c_{12} - k_{-7}c_8c_{11} - k'_{16}c_8 + k_{-16}c_1c_{11} - 0.5\,k_{12}c_8 + 0.5\,k'_{-13}c_{10}c_{11} + k'_5c_2c_{13}$$

$$\mathrm{d}c_9/\mathrm{d}\tau = -k'_1c_2c_9 + k_\mathrm{A}c_8c_{11} + k_\mathrm{E}c_9c_{11}$$

$$\mathrm{d}c_{10}/\mathrm{d}\tau = 0.5k'_{12}c_8 - 0.5k'_{-13}c_{10}c_{11} - k'_{14}c_2c_{10} + k_\mathrm{B}c_1$$

$$\mathrm{d}c_{12}/\mathrm{d}\tau = k'_1c_2c_9 - k'_7c_{12} + k_{-7}c_8c_{11} - 0.5k'_3c_{12} + 0.5k'_{-4}c_{11}c_{13}$$

$$\mathrm{d}c_{13}/\mathrm{d}\tau = 0.5k'_3c_{12} - 0.5k'_{-4}c_{11}c_{13} - k'_5c_2c_{13}$$

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

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

where c_1 is the concentration of $\mathrm{CF_3{-}CClH_2}$; c_2, HF, c_3, $\mathrm{CF_3{-}CFH_2}$; c_4, $\mathrm{CF_3{-}CH_3}$; c_5, $\mathrm{CF_3{-}CCl_2H}$; c_6, $\mathrm{CF_3{-}CFClH}$; c_7, $\mathrm{CF_3{-}CF_2H}$; c_8, $\mathrm{CF_2Cl{-}CClH_2}$; c_9, $\mathrm{C_2HCl_3}$; c_{10}, $\mathrm{CF_2{=}CClH}$; c_{11}, HCl; c_{12}, $\mathrm{CFCl_2{-}CClH_2}$; c_{13}, $\mathrm{CFCl{=}CClH}$; $k'_i = k_i \cdot [\mathrm{CrF_3}]$, $k_\mathrm{A} = 2(k'_{14}k_{13}k_{12}/k'_{-13}k_{-14})$, $k_\mathrm{B} = k_{-1}k_{-10}/(k'_{10} + k_{11})$, $k_\mathrm{C} = k_{-3}k'_{-4}/(k_{-3} + k_4)$, $k_\mathrm{D} = k_{-3}k'_3/(k_{-3} + k_4)$, and $k_\mathrm{E} = k_{-14}k'_{14}k'_{-15}/k_{15}k'_{-13}$.

When searching for the constants of the kinetic model, the LSODA technique was used for numerical integration of a set of ordinary differential equations.[17a]

The kinetic constants found in this way are summarized in Table 2.

The kinetic model describes adequately processes (*1*) and (*2*) (Scheme 3) in the following range of operating parameters: temperature 175—420 °C; reagent molar ratio HF : $\mathrm{C_2HCl_3}$ = (3.4—13.6) : 1; HF : $\mathrm{C_2H_2ClF_3}$ = (4—20) : 1.

Analysis of the process in terms of the kinetic model has shown that the optimal conditions for stages (*1*) and (*2*)

Table 2. Parameters of the Arrhenius equation for the preparation of 1,1,1,2-tetrafluoroethane from trichloroethylene

k_i	ln*A*	E_a /kJ mol^{-1}
k'_1	33.8	125.2
k'_3	38.7	146.1
k'_{-4}	58.7	207.7
k'_5	46.7	162.4
k'_7	16	66.5
k_{-7}	23	126.0
k'_{12}	17	83.7
k'_{-13}	23.7	83.7
k'_{14}	12.2	41.9
k'_{16}	16.5	70
k_{-16}	19.5	85
k'_{17}	11.7	76.6
k_{-17}	15.6	51.1
k'_{18}	26.2	148.5
k'_{20}	33	74.6
k_{-20}	30	115
k'_{21}	17	97
k_{-21}	26.5	103
k_A	43	209.3
k_B	29.5	188.4
k_C	8.5	20.9
k_D ~0	—	—
k_E ~0	—	—

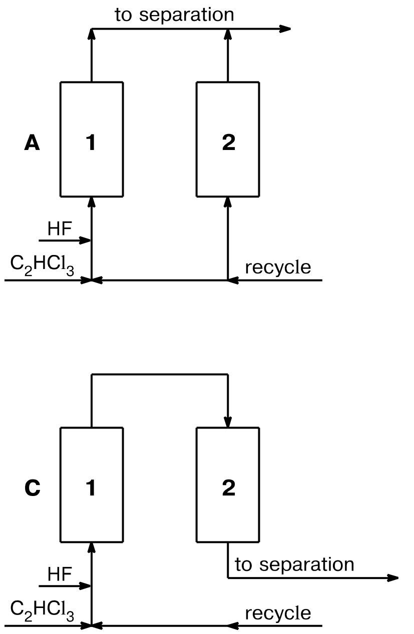


Fig. 1. Models of two-reactor block diagrams for the synthesis of 1,1,1,2-tetrafluoroethane.

(Scheme 3) are appreciably different (the exothermic and endothermic processes, stage (1) is better carried out at a lower temperature than stage (2), *etc.*). Therefore, it is expedient to produce chladone 134a in a two-reactor mode. The best arrangement of the reaction unit was chosen using the mathematical model of a fixed-bed adiabatic reactor with the chromium magnesium fluoride catalyst:

$$u \cdot dC_i/dx = R_i,$$

$$\rho \cdot C_p \cdot u \cdot dT/dx = \Sigma(\Delta H_j r_j),$$

where $R_i = \Sigma\nu_i \cdot r_j$ is the rate of variation of the concentration of an ith component due to chemical reactions, mol $(m^3\ s)^{-1}$; ν_i is the number of moles of an ith component participating in a jth reaction; r_j is the rate of the jth reaction, mol $(m^3\ s)^{-1}$; C_i is the concentration of an ith component in the gas mixture, mol m^{-3}; x is the reactor length, m; T is the temperature, K; ρ is the density of the gas mixture depending on the component concentrations and the temperature ($\rho(C, T)$), kg m^{-3}; u is the linear velocity of the mixture, m s^{-1}; C_p is the average heat capacity of the mixture, J $(kg\ K)^{-1}$; ΔH_j is the heat of the jth reaction, J mol^{-1}.

We considered four block charts of the reaction unit, which are shown in Fig. 1. The calculations performed in terms of the above mathematical model demonstrated that the maximum capacity with respect to chladone 134a is ensured by pattern **A** [18] (Table 3).

According to pattern A, hydrogen fluoride, trichloroethylene, and some of the recycled mixture (for maintenance of the temperature conditions) with a total amount of HF and 1,1,1-trifluorochloroethane equal to >99% are fed to the first reactor, while the main bulk of the recycled mixture with the same composition is fed to the second reactor; the reaction unit effluents are combined and routed to the isolation of hydrogen chloride, light-end products, and 1,1,1,2-tetrafluoroethane, while high-boiling compounds are recycled to the reaction unit.

Table 3. Analysis of the reaction unit of the synthesis of 1,1,1,2-tetrafluoroethane (TFE)

Reaction unit	Capacity for TFE, kg s^{-1}
A	0.0268
B	0.0237
C	0.0218
D	0.0238

Note. The calculations were carried out for the following input data: HF rate 60.86 kg g;^{61} C_2HCl_3 rate 97.54 kg g^{-1}; recycle rate 1121.5 kg g^{-1}; for pattern A: recycle to the first reactor, 166.44 kg g^{-1}; recycle to the second reactor 955.07 kg g^{-1}; temperature at the first reaction inlet 170 °C; temperature at the second reaction inlet 400 °C.

A typical flow diagram for the synthesis of non-ozone-depleting chladones by gas-phase catalytic hydrofluorination (for example, of pentafluoroethane) has been developed.[19] For plasma etching in microelectronics, a process for the synthesis of chladone 116 has been developed;[20] and a process for chladone 23 synthesis has been elaborated for filling of low-temperature refrigerating machines.[22]

On the basis of this research, production processes of non-ozone-depleting chladones have been commissioned

Table 4. Production of ODS substitutes at Russian Federation plant (ton per year)[1]

Substitute ODS	Manufacturer*	Consumer sector	Available facilities (t/y)
Non-ozone-depleting substances			
GFU-134a	Galogen	Refrigerants, aerosol propellants, solvents, foaming agents	Production is planned
GFU-23	ROZ	Refrigerants, fire-extinguishing agents	200
GFU-32	Galogen	Refrigerants	Production is planned
GFU-152a	Kaustik	Refrigerants, aerosol propellants	4000
GFU-143a	KCKK	Refrigerants	100
GFU-125	Galogen	Refrigerants, fire-extinguishing agents	1000
GFU-227ea	RSC AC	Refrigerants, aerosol propellants,	50
	KCKK	solvents, fire-extinguishing agents	100
FU-218	KCKK	Refrigerants,	120
	AEP	aerosol propellants,	100
	Galogen	fire-extinguishing agents, gases for electronics	40
FU-3110	AEP	Refrigerants, aerosol propellants, fire-extinguishing agents, gases for electronics	100
FU-C318	KCKK	Refrigerants	100
	Galogen		40
FU-116	AEP	Refrigerants, gases for electronics, solvents	100
Transition chladones			
GKhFU-141b, 142b	Altaikhimprom	Solvents, foaming agents	3000
GKhFU-142b	KCKK	Foaming agents	2000
GKhFU-22	VOKKO	Refrigerants,	12000
	KCKK	aerosol propellants,	20000
	Galogen	intermediate for the production of fluoroplastics	12000
GKhFU-21	Galogen	Refrigerants, aerosol propellants	100
Mixtures**			
S10M1 (GKhFU-21, -22, -142b)	Astor	Refrigerants	1000
S10M2 (GKhFU-21, -22, GFU 134a)			
GKhFU 22/-142b	KCKK	Foaming agents	1000
C 1 (GFU 152a/ isobutane)	Kaustik	Refrigerant	200

* Designations: Astor stands for closed joint-stock company Astor (St-Petersburg); Altaikhimprom is the open joint-stock company Altaikhimprom (Yarovoe); AEP is the open joint-stock company Angarsk Electrolysis Plant (Angarsk); BOKKO is the open joint-stock company Khimprom (Volgograd); Galogen stands for the open joint-stock company Galogen (Perm´); Kaustik is the open joint-stock company Kaustik (Volgograd); KCKK is the open joint-stock company Konstantinov Kirovo-Chepetsk Chemical Integrated Plant" (Kirovo-Chepetsk); RSC AC means the FSUE RSC "Applied Chemistry" (St.Petersburg); ROZ is the open joint-stock company Redkino Pilot Plant (Redkino).

** Mixtures are composed of substances included in Table 2.

and continue to be designed in the Russian Federation (Table 4).

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