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Preparation of Higher $\alpha,\alpha,\alpha,\omega$-Tetrachloroalkanes in a Flow Apparatus

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Earlier, the possibility of synthesizing higher tetrachloroalkanes at pressures of 100–150 atm was shown, and the quantitative dependence of their content on the pressure and relative concentration of ethylene was evaluated ([1]). The present article describes a flow apparatus for the continuous preparation of higher tetrachloroalkanes and specifies the conditions for carrying out the process.

The effect of temperature and reaction time was studied in rocking autoclaves equipped with electric heating and a water jacket, which made it possible to regulate the temperature to within 1°. The pressure was kept constant by feeding ethylene into the autoclave as it was consumed. The discrepancies between the amounts of ethylene measured by two independent methods were $±$3.3% in each individual experiment and 0.2% for a series of 17 experiments. Azodiisobutyronitrile was used as the initiator, at a concentration of 1 g per 1 liter of autoclave volume. The mixture of tetrachloroalkanes was separated by rectification under vacuum.

Table 1

Experiment no.	Temperature, °C	Time, min	Conversion of CCl_4, %	C_5	C_7	C_9	$C_{>9}$
1	90	15	15	34.5	27	23	15.5
2	90	30	24.5	38.3	30.8	18.5	12.5
3	90	60	36	32	31	17	18.5
4	90	120	47	33	31	16	18.5
Average	90			34.5	30	19	16.3
5	100	15	24	41	31.7	13.7	11.3
6	100	30	30	43	29.7	14	11
7	100	60	31.3	41.5	31	15	10.5
8	100	120	33.5	42.5	28	15.5	11.5
Average	100			41.8	30.4	13.4	11
9	80	60	28	16	21	17	46

Experiment no.	Temperature, °C	Time, min	Conversion of CCl_4, %	C_5	C_7	C_9	$C_{>9}$
10	50	120	45	17	24	18	41
11	90	30	31	–	–	–	–
12	90	60	54	20.8	26	19	34.5
13	90	120	66.5	21	26.2	16.5	36.5
14	100	15	30	–	–	–	–
15	100	30	41	–	–	–	–
16	100	60	44	33	23	14	30
17	100	120	44	–	–	–	–

Notes: 1. Experiments nos. 1-8: autoclave 0.35 l, pressure 120 atm, ethylene/CCl_4 $= \frac{3.2}{0.8} = 4$ mol/mol; experiments nos. 9-17: autoclaves 0.5 l and 2.7 l, pressure 150 atm, ethylene/CCl_4 = 10 mol/mol.
2. In experiments nos. 5-8 at 100°, 2.5-3% tetrachloropropane (C_3) was isolated.

Table 1 and Fig. 1 show the averaged results of a large number of experiments, from which it is evident that at 100° the reaction is practically complete in 20-30 min, but the conversion of CCl_4 is considerably lower than at 90°. It has been established that the composition of the mixture of tetrachloroalkanes depends on temperature: as the latter is increased, the content of the lower (C_5) telomers increases and the amount of higher (C_9 and $C_{>9}$) telomers decreases.

The experiments described here and earlier [1] were carried out in autoclaves of various diameters (35, 50, and 100 mm). No appreciable influence of the reactor dimensions on the conversion and composition was found. In a special series of experiments

Table 2

Temp., °C	Press., atm	Duration, h	Ethylene/CCl_4, mol/mol	Conversion of CCl_4, %	C_3	C_5	C_7	C_9	$C_{>9}$
Autoclave 0.5 l, diameter 50 mm									
90	120	1	2.2	43	5	47	28	12	8
90	120	1	3.3	33	2	40	32	16	10

Temp., °C	Press., atm	Duration, h	Ethylene CCl_4, mol/mol	Conversion of CCl_4, %	C_3	C_5	C_7	C_9	$C_{>9}$
90	120	1	4.5	42	–	38.5	30	16.5	15
90	150	1	9.7	51	–	21	24	21	34
100	120	0.5	4.1	30	3	42	30	14	11
100	120	1	3.9	31	2.5	41.5	31	15	10
Autoclave 0.5 l, with 10$×$10 mm packing									
90	120	1	2.2	41.5	5	45.5	30	12	7.5
90	120	1	3.7	36.5	2.5	41	29	14.5	13
90	120	1	4.7	43	–	40.5	30	15.5	14
90	150	1	10	55	–	21	24	18	37
Coil, volume 70 ml, diameter 4 mm*									
100	120	0.5-1	2.6	28.8	–	–	–	–	–

* The reaction was conducted in flow. In 3 h, 180 g of CCl_4 and 84.5 g of ethylene were passed through; 80 g of tetrachloroalkanes was obtained.

in a flow reactor 4 mm in diameter and in a 0.5-l autoclave filled with 10$×$10 mm glass-ring packing, no substantial, regular difference was likewise found in comparison with experiments in the same autoclave under identical conditions but without packing (Table 2).

With simultaneous charging of the entire amount of initiator, its complete utilization is not achieved; temperature jumps are also possible, lowering the conversion. Gradual feeding of the initiator during the process should create a uniform concentration of initial radicals, ensure more complete utilization of the initiator, and increase the conversion. This assumption was tested in exper-

iments with uniform feeding of the initiator (0.53 g per 38 ml of CCl_4) through a capillary tube 1 mm in diameter into a rocking autoclave containing ethylene and CCl_4 (3 mol/mol) at 120 atm. Table 3 shows that, with prolonged, uniform feeding of the initiator, the conversion increased 1.5-fold in comparison with short-term charging.

Table 3

Initiator feed time, min	Temperature, °C	Conversion of CCl_4, %	Specific gravity of telomer mixture
8	100	24	1.254
30	100	37	1.263
5	100–115	19	1.261
30	100–115	29	1.263

The flow installations for telomerization described in the literature [2–4] differ substantially in the method of returning unreacted ethylene to the reactor and in the construction of the latter. Taking into account the critical parameters of ethylene and the data of Efremova and Leont' eva [5], a closed system for circulating ethylene under a pressure of 40–60 atm, at a separator temperature of 90–120° [6], was proposed and calculated. The circulation scheme is improved if CCl_4 is fed not into the reactor but into the mixer [4]. In this case

the critical temperature of the mixture is raised and the operation of the circulation pump is improved.

The data obtained in this work were used in creating a continuous flow installation for the synthesis of higher tetrachloroalkanes, the schematic diagram of which is shown in Fig. 2. The stainless reactor, made of standard tubes 58/50 mm in diameter, has six sections with intermediate outlets and thermocouple sleeves in each section. Such a design makes it possible to study the dynamics of the process and, in order to increase the conversion and ensure a calm course of the reaction, to feed the initiator uniformly into all sections.

In this installation a series of continuous experiments was carried out on the synthesis of higher tetrachloroalkanes (TXA), aimed at obtaining the maximum amount of the C_9—C_{15} fraction.

Experimental conditions: pressure 140–150 atm., temperature 90–95°, initiator concentration 8–10 g/l CCl_4, which corresponds to approximately 0.5–0.8 g/l of reactor volume, relative ethylene concentration 10–11.5 moles/mole CCl_4. Table 4 gives the results of 7 experiments, each 4–8 hours in duration, under steady-state conditions.

Fig. 1. Effect of time and temperature on the conversion of CCl_4 at a relative ethylene concentration of 4 (a) and 10 (b) moles per 1 mole of CCl_4.

Fig. 2. Diagram of the flow installation

Figure 1: Fig. 2. Diagram of the flow installation

Table 4

No.	CCl_4 consumption, kg	C_2H_4 consumption, kg	Total consumption, kg	Reaction mass, quantity, kg	Reaction mass, specific gravity	TXA content, kg	TXA content, %	C_5, %	C_7, %	C_9, %	$C_{>9}$, %
1	9.7	2.3	12.0	11.0	1.35	5.3	48	22	26	22	30
2	20.4	5.9	26.3	26.5	1.39	12.2	46	25	22	15	38
3	11.4	1.9	13.3	13.2	1.35	7.2	55	22	25	17	36
4	11.8	3.5	15.3	15.7	1.38	7.7	49				
5	12.9	3.1	16.0	16.3	1.38	7.6	46	23	20	22	45
6	13.2	3.7	16.9	16.1	1.35	8.3	51				
7	18.3	5.0	23.3	22.1	1.36	11.6	52	25	23	17	35
Total	**97.7**	**25.4**	**123.1**	**120.9**	**1.365**	**59.9**	**49.6**				

The ethylene content in the reaction products, according to analytical data, is 41%, or 24.5 kg, which gives a discrepancy with the charged amount of 3.5% with total material losses of 1.8%. The composition of the telomer mixture agrees quite satisfactorily with the data from the autoclave experiments (see Table 1). From a mixed sample of the residues after rectification on the column there was isolated

fraction of higher tetrachloroalkanes C_{11}–C_{15} in an amount of 23% in autoclave experiments and 18-22% in flow experiments (calculated on the initial mixture of telomers), which is somewhat lower than the maximum possible amount ([1]).

The absence of appreciable losses, the good agreement of the ethylene balance, and the small deviations of the results of individual experiments from the mean values

Fig. 2. Diagram of the flow installation: **1** –gas meter, **2** –compressor, **3** – CCl_4 measuring vessel, **4** –metering pump, **5** –cooler-mixer, **6** –sampling vessel, **7** –circulating pump, **8** –reactor, **9** –separator, **10** –TKhA receiver, **11**, **12** – gas counters, **13** –high-pressure flowmeter, **14** –adsorber, **15** –thermocouples, **16** –intermediate outlets; **a** –high pressure (50-150 atm.), **b** –low pressure (0.1-0.3 atm.)

show that the process of synthesizing higher tetrachloroalkanes is stably reproduced in the installation at pressures below 150 atm. under conditions of increased concentrations of ethylene and initiator.

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Note: Figure translations are in progress. See original paper for figures.