Synthesis and application of ω-bromoperfluoroalkylvinyl ethers

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Report 3. Production α,ω-dibromoperfluoroalkanes as a raw material in synthesis of

ω-bromoperfluoroalkylvinyl ethers.

Report 1 describes a new method of synthesis ω-bromoperfluoroalkylvinyl ethers (BrAVE) from α,ω-dibromoperfluoroalkanes (DIBAF), covalent fluorosulfates and hexafluoropropylene oxide according to the scheme:

From this it follows that for synthesis of BrAVE it is necessary to have DIBAF with various chain length.

There is industrial production only of dibromofluoromethane (R12B2) and 1,2-dibromotetrafluoroethane (R-114 B2). 1,4-Dibromooctafluorobutane (R-318 B2) may be separated in the production of R-114 B2 in a small amount as an admixture.

This paper describes DIBAF synthesis as telomerization of tetrafluoroethylene with R-12 B2 or R-114 B2.

General provisions.

The data obtained by us allow to conclude that reactions of TFE with DIBAF are based on ability of the latter to homolytic breaking the bond C-Br followed by formation of the appropriate organofluorine radical and its subsequent addition to the fluoroolefin:

$$Br(CF_2)_nB \rightleftharpoons Br(CF_2)_n* + Br* \quad (1)$$

$$Br(CF_2)_n*+mCF_2 = CF_2 \rightarrow Br(CF_2)_n(CF_2CF_2)_m* \quad (2)$$

$$Br(CF_2)_n(CF_2CF_2)_m*+ B \rightleftharpoons Br(CF_2)_n(CF_2CF_2)_mBr \quad (3)$$

At the same time, apparently, the reactions connected with TFE bromination take place:

$$B_2 \rightleftharpoons 2Br * \quad (4)$$

$CF_2 =CF_2 + Br^* \rightarrow CF_2CF_2Br^*$ (5)

$CF_2 =CF_2 + 2Br^* \rightarrow BrCF_2CF_2B \rightleftharpoons CF_2CF_2Br^* + Br^*$ (6)

$CF_2CF_2 Br + CF_2 =CF_2 \rightarrow (CF_2CF_2)_mBr$ (7)

$Br(CF_2)_m + (CF_2CF_2)_mBr \rightarrow Br(CF_2)_n(CF_2CF_2)_mBr$ (8)

As regards other theoretically possible reactions such as recombination of radicals:

$Br(CF_2)_n^* + Br(CF_2)_n \rightarrow Br(CF_2)_{2n}Br$ (9)

$Br(CF_2CF_2)_m^* + Br(CF_2CF_2)_m^* \rightarrow Br(CF_2CF_2)_{2m}Br$ (10)

$Br(CF_2)_n(CF_2CF_2)_m + Br(CF_2)_n(CF_2CF_2)_m^* \rightarrow Br(CF_2)_{2n}(CF_2CF_2)_{2m}Br$ (11)

further homolytic decay of the bond C-Br in reaction products 6,7,8,9 and their subsequent interaction with other organofluorine radicals etc., the experimental results unambiguously prove that the share of these reactions is negligibly small in comparison with reactions 1,2,3,4,5,6, though one could assume by analogy with reactions 7,8,9 that the share of reactions 5,6 is also small.

The chain breaking takes place in case of interaction of radicals I and II with atomic bromine and as a result of recombination of radicals I and II:

$Br(CF_2)_n(CF_2CF_2)_m^* + Br^* \rightarrow Br(CF_2)_n(CF_2CF_2)_mBr$

$Br(CF_2)_n(CF_2CF_2)_m^*(II) + Br(CF_2)_n^*(I) \rightarrow Br(CF_2)_{2n}(CF_2CF_2)_mBr$

Reactions 1,3 are reversible, this can be used in specific technological processes for preferable synthesis of DIBAF with a necessary chain length.

Further dissociation of radical I with formation of the appropriate fluorocarbon was not practically observed.

2. Synthesis α,ω-dibromoperfluoroalkanes with odd number of carbon atoms.

The reaction was studied on the example of TFE interaction with difluorodibromomethane (R-12 B2) and difluorobromochloromethane (R-12 B1).

Investigations were carried out in a flow gas phase reactor at atmospheric pressure and at various ratios of reagents, various temperatures and contact time. Dibromodifluoromethane was fed by bubbling gaseous TFE through it. The necessary ratio of components was achieved by adjustment of R-12 B2 temperature, and R-12 B1 was fed through a gas mixer at the same time with TFE. Formation of telomerization products during the interaction of TFE and R-12 B1 at a temperature up to 600^{o}C was not observed. At a contact time of 15 sec and a temperature of up to 180^{o}C interaction of TFE with R-12B2 is practically absent either. Some examples of specific carried out syntheses of *1,3-dibromohexafluoropropane* are given in Table 1.

Table 1

NN	Temperature, ^{0}/p>	Contact time, sec	Ratio of 12B2:TFE	TFE conversion, %	DIBAF yield (%)		
					ñ=3	ñ=5	ñ=7
1	300	8	2:1	3,4	88	6	traces
2	350	8	2:1	10,6	89	6	traces
3	400	8	2:1	15,4	91	5	traces
4	450	8	2:1	23,5	92	3	0,4
5	500	8	2:1	26,5	93	4	0,8
6	450	6	3:1	34,2	95	3	traces
7	480	6	3:1	27,1	96	2	traces
8	480	8	2:1	25,1	90	4	0,9
9	480	10	1:1	28,8	79	6	3

The given examples as a whole are typical for the given reaction, i.e.:

- DIBAF formation with even number of carbon atoms is practically absent;
- An increase in the temperature and in the share of the starting dibromoalkane increase a little the total DIBAFyield;
- An increase in the contact time and in the TFA share allows to increase the yield of DIBAF with a longer chain;
- At increasing dibromalkane excess, optimal DIBAF yield and TFE conversion is attained at a lower temperature.

3. Synthesis α,ω-dibromoperfluoroalkanes with even number of carbon atoms.

The process was studied as interaction of R-114B2 with TFE at the same laboratory-scale plant that the reaction of R-12B2 with TFE under following conditions:

- a temperature of 200-750^{0}C
- a contact time of 5-25 sec;
- a molar ratio of R-114 B2:TFE in the range of 0.5:1 - 4:1
- thermostating accuracy within +0.1^{0}C.

Some results on synthesis of 1,4-dibromooctafluorobutane are presented in Table 2.

NN	Temperature, ^0C	Contact time, sec.	Ratio of 114B2: TFE	TFE conversion,%	DIBAF yield %		
					ñ=4	ñ=6	ñ=8
1	600	13,6	1:1	28	49	13	1,1
2	590	10,1	1,1:1	31	50	13	0,5
3	610	9,1	2:1	48	63	10	1,4
4	575	8,8	2,17:1	56	55	11	2,4
5	580	8,2	2,3:1	53	64	9	1,5
6	600	7,6	2,6:1	57	66	10	-
7	580	6,2	3,4:1	47	73	8	-

It is evident from the experimental data that:

- TFE conversion and the yield of goal compounds increase along with an increase in the starting dibromoalkane excess;
- An optimal temperature range is 580-630^{0}C;
- A share of low molecular DIBAF is increasing with an increase of the starting dibromoalkane excess;
- It is necessary to decrease the contact time at higher temperatures;
- TFE homopolymerization takes place in some experiments;
- Derivatives with even number of carbon atoms are practically absent.

4. Influence of the concentration of bromine atoms on the composition of the reaction products.

It is seen from the above-mentioned total scheme of DIBAF synthesis that the concentration of bromine atoms affects significantly the composition of the reaction products. The bromine atoms can be considered as initiators and chain length regulators (reactions 1,3,4,5,6) especially because the dissociation energy of the bonds C-Br and Br-Br is significantly lower than that of the C-F and C-C bonds (87,45,129,and 144 kcal/mole respectively).

The influence of the concentration of bromine atoms on the telomerization reaction of fluoroolefins with fluorinated bromoalkanes is given as the reaction of TFE with R-114 B2.

Since bromine readily reacts with TFE under lighting in gas phase as well as in liquid phase, a preliminarily prepared mixture of R-114B2 and bromine (the content of the latter was up to 10%) was placed in an opaque vessel through which TFE was then bubbled. The investigations were carried out under the same conditions as those without bromine.

The experimental data at a temperature of 600^{0}C and a contact time of 9sec are given in Table3.

NN	Ratio of 114B2: TFE:Br	TFE conversion,%	DIBAF yield %		
			ñ=4	ñ=6	ñ=8
1	2:1:0,07	55	52	10	3
2	2:1:0,17	54	64	9	2
3	2:1:0,36	59	77	6	1

An addition of bromine up to 2% actually does not affect the process. An increase of the bromine concentration in a range of 5-10 wt% leads not only to an increase in the total DIBAF yield but also to an increasing share of low molecular derivatives. This may be used for the technical purposes to increase the process selectivity.

Conclusions.

As it is seen from the given experimental data, the task to produceα,ω-dibromoperfluoroalkanes with different chain length has been actually solved.

If necessary, the developed synthesis method can be readily applied in industry.

It is necessary also to note that the goα,ω-dibromoperfluoroalkanes are raw materials not only for the BrAVE synthesis but also in production of other functional fluorine compounds (acids, amines, acid halides etc.) because both bromine atoms are reactive enough and can be readily replaced with the appropriate functional groups.