

Synthesis and Properties of Di(polyfluoroalkyl) Peroxydicarbonates

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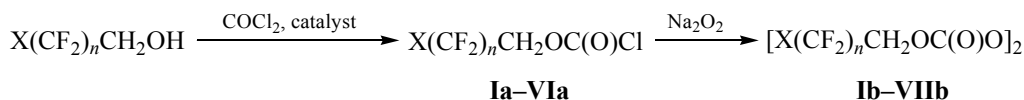
Abstract—Synthesis of di(polyfluoroalkyl)peroxydicarbonates $[X(CF_2)_nCH_2OC(O)O]_2$, where $X = H, F$; $n = 1, 2, 4, 6$ (yield 80%) involves the step of the chloroformate formation (yield up to 93%) via the phosgenation of polyfluorinated alcohols followed by the reaction with sodium peroxide. The rate constant of monomolecular decomposition k_{term} was found to decrease as the polyfluoroalkyl groups were incorporated into the peroxide: it equaled 3.30 and 3.10 s^{-1} for $X = H$, $n = 2$ and 4, respectively, and 7.36 s^{-1} for di-*n*-butylperoxydicarbonate. The new peroxides are a source of the polyfluoroalkoxy radicals and nano-modifiers of the polymers to improve their heat resistance and light stability.

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Peroxydicarbonates are widely used for the polymerization of vinyl monomers [1]. A disadvantage of these peroxides is their high explosiveness and a low thermal stability. Introduction of polyfluoroalkyl fragments in nano-amounts into the macromolecular systems enhances the heat resistance and stability against light of the polymeric materials [2]. In this connection the works on the synthesis of polyfluoro-

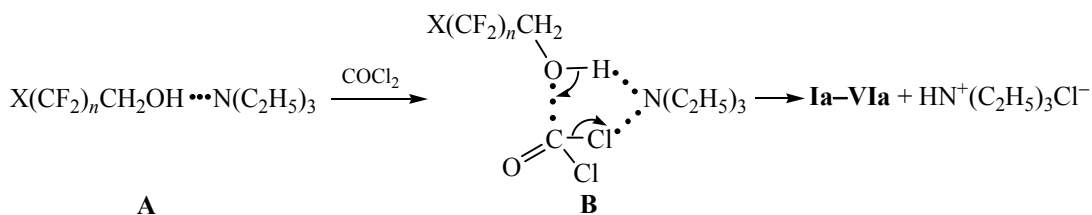
alkyl peroxycarbonates as the nano-modifiers of the polymer systems are actual [3].

In this paper we consider a two-step synthesis of di-(polyfluoroalkyl) peroxydicarbonates including a catalytic phosgenation of polyfluorinated alcohols [4] and their reaction with the freshly prepared aqueous solution of sodium peroxide.



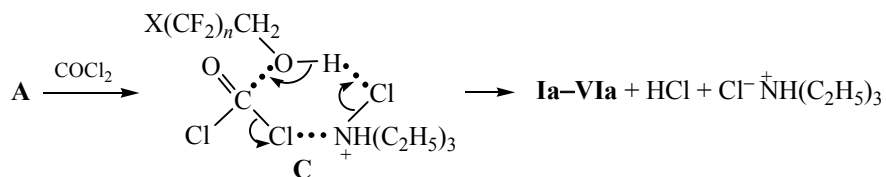
The phosgenation of the polyfluorinated alcohols was performed in the presence of catalytic amounts of pyridine, triethylamine or *N,N*-dimethylformamide (DMF) (Table 1). These compounds show similar catalytic

activity that suggests common mechanism of the chloroformate formation. The associate **A** of the polyfluorinated alcohol with amine or acids amide form a polar complex **B** with phosgene leading to the chloroformate formation:



Triethylamine hydrochloride may also participate in the catalysis of the reaction of polyfluorinated alcohol

with phosgene to form a polar six-membered structure **C**:



The association of the polyfluorinated alcohols with triethylamine or DMF was studied by means of the IR and NMR spectroscopy [5–7]. Owing to high acidity of alcohols, the hydrogen bonding in the associate is rather strong. This facilitates the further complexation with phosgene and the reaction proceeding. The polyfluoroalkyl chloroformates yields are 83–93%. They are low-boiling liquids with a density of 1.48–1.72 g cm⁻³ (Table 2).

The nucleophilic substitution of *tert*-butylperoxy groups in polyfluoroalkyl chloroformates with chlorine have been described earlier [5]. The reaction of chloroformates with *tert*-butylhydroperoxide was carried out in the presence of pyridine or sodium hydroxide at –5 to 0°C to obtain *tert*-butylperoxypolyfluoroalkyl carbonates in yields of 65–80%.

In this work the polyfluoroalkyl chloroformates were peroxygenated by the solution of sodium peroxide freshly prepared from 30–50% aqueous sodium peroxide and 13–17% aqueous sodium hydroxide. To prevent the peroxydicarbonate decomposition, the reaction temperature was maintained in the initial period at about –5 to 0°C and then raised to 15–20°C. The organic layer was separated, washed with water, dried with anhydrous sodium sulfate and kept at a reduced pressure for 30–40 min. The individuality of di(polyfluoroalkyl) peroxydicarbonates obtained was established by TLC (Table 3). Note that the yield of peroxydicarbonates decreases as the length of perfluoroalkyl chain in the starting chloroformates increases. Di(polyfluoroalkyl)peroxydicarbonates are heavy liquids with the density 1.62 to –1.78 g cm⁻³, except for trifluoroethyl peroxydicarbonate (1.43 g cm⁻³).

Table 1. Effect of the reactants ratio and the phosgenation parameters on the yield of polyfluoroalkyl chloroformates **Ia–IIIa**, **Va** and **VIa**

Comp. no.	Catalyst		Alcohol:phosgene	T, °C	Time, h	Yield, %
	compound	mol				
Ia	DMF	0.07	1:1.4	50	3.0	90
IIa	DMF	0.05	1:1.2	90	1.5	86
	DMF	0.1	1:1.5	95	2.0	93
	Pyridine	0.03	1:1.2	80	2.5	87
IIIa	Pyridine	0.1	1:1	80	3.0	83
	DMF	0.1	1:1.2	90	1.5	88
Va	TEA	0.08	1:1.3	70	2.0	88
VIa	TEA	0.04	1:1.25	90	2.0	87

Table 2. Polyfluoroalkyl chloroformates

Comp. no.	Compound	bp, °C (mm Hg)	n_D^{20}	d_4^{20}
Ia	2,2,2-Trifluoroethyl chloroformate	40 (165)	1.3210	1.4896
IIa	1,1,3-Trihydroperfluoropropyl chloroformate	35 (32)	1.3510	1.5179
IIIa	1,1,5-Trihydroperfluoropentyl chloroformate	50 (11)	1.3376	1.6475
IVa	1,1-Dihydroperfluoropentyl chloroformate	36 (15)	1.3182	1.6200
Va	1,1-Dihydroperfluoroheptyl chloroformate	59 (13)	1.3188	1.7105
VIa	1,1,7-Trihydroperfluoroheptyl chloroformate	63 (3)	1.3338	1.7240

Table 3. Di(polyfluoroalkyl) peroxydicarbonates **Ib–VIb**^a

Comp. no.	X(CF ₂) _n CH ₂	Yield, %	R _f	d ₄ ²⁰	n _D ²⁰	MR _D		Elemental analysis						
						found	calculated	Found, %			Formula	Calculated, %		
								C	F	O _{act}		C	F	O _{act}
Ib	CF ₃ CH ₂	75	0.73	1.4338	1.3298	40.53	40.62	24.91	39.82	5.57	C ₆ H ₄ O ₈ F ₆	25.17	39.86	5.59
IIb	H(CF ₂) ₂ CH ₂	78	0.75	1.6214	1.3548	47.01	46.98	27.40	43.37	4.56	C ₈ H ₆ O ₆ F ₈	27.42	43.42	4.57
IIIb	H(CF ₂) ₄ CH ₂	80	0.78	1.7167	1.3362	66.47	66.57	25.87	55.07	2.78	C ₁₂ H ₆ O ₆ F ₁₆	26.18	55.27	2.90
IVb	F(CF ₂) ₄ CH ₂	66	0.76	1.7110	1.3192	67.82	67.82	24.04	58.16	2.64	C ₁₂ H ₆ O ₆ F ₁₈	24.57	58.36	2.73
Vb	F(CF ₂) ₆ CH ₂	68	0.77	1.7330	1.3095	87.41	87.41	24.13	62.80	1.97	C ₁₆ H ₄ O ₆ F ₂₆	24.42	62.84	2.03
VIb	H(CF ₂) ₆ CH ₂	79	0.79	1.7828	1.3308	86.16	86.16	25.01	59.27	2.10	C ₁₆ H ₆ O ₆ F ₂₄	25.60	60.08	2.13

^a **Ib**, di(2,2,2-trifluoroethyl) peroxydicarbonate, **IIb**, di(1,1,3-trihydroperfluoropropyl) peroxydicarbonate, **IIIb**, di(1,1,5-trihydroperfluoropentyl) peroxydicarbonate, **IVb**, di(1,1-dihydroperfluoropentyl) peroxydicarbonate, **Vb**, di(1,1-dihydroperfluoroheptyl) peroxydicarbonate, **VIb**, di(1,1,7-trihydroperfluoroheptyl) peroxydicarbonate.

In the IR spectra of di(polyfluoroalkyl) peroxydicarbonates there are two absorption bands at 1778±2 and 1807±3 cm⁻¹, corresponding to the stretching vibration of carbonyl group in the unsubstituted peroxydicarbonates [1, 3]. This indicates that the polyfluoroalkyl groups located in β-position relative to the peroxydicarbonate group do not affect appreciably the spectral characteristics of the latter. The stretching vibrations of the O–O bond in di(polyfluoroalkyl) peroxydicarbonates appear in the range of 845–850 cm⁻¹. The stretching vibrations of the C–O–C fragment are observed at 1041–1094 cm⁻¹, which corresponds to the published data [8].

In the ¹H NMR spectra of all synthesized peroxydicarbonates [X(CF₂)_nCH₂OC(O)O]₂ the signal of terminal proton of HCF₂-group appears as a triplet of triplets at 5.8±0.05 ppm (^aJ_{HF} 52 Hz), each component of which is split into a triplet with a spin-spin coupling constant with the β-fluorine atom ^βJ_{HF} 5.5 Hz. The signal of two CF₂CH₂-protons is seen as a well-resolved triplet at 4.6±0.03 ppm with the spin-spin coupling constant J_{HF} 5.5 Hz.

The kinetics of thermal decomposition of di(polyfluoroalkyl)peroxydicarbonates in benzene and ethylbenzene was studied at the initial peroxide concentration of 4×10⁻² mol l⁻¹, which allows minimizing the induced decay processes involving the free radicals from the peroxide. The thermolysis rate

constants, half-life (τ_{1/2}) and activation energy for **IIb** and **IIIb** in comparison with a widely used di(*n*-butyl) peroxydicarbonate **VII** are presented in Table 4. The introduction of perfluorinated carbon chains into the dialkyl peroxydicarbonate **IIb** structure and the elongation of this chain by more than two times in **IIIb** reduce the rate constant of thermolysis in benzene compared with the unsubstituted peroxide **VII**: *k*_{term} at 70°C for **IIb**, **IIIb** and **VII** are 3.30, 3.10, and 7.36 s⁻¹, respectively. The half-life of the peroxide at 70°C varies in the following order: **IIb** 35 min, **IIIb** 38 min, **VII** 16 min.

The half-life, rate constant of the monomolecular decomposition, and the activation energy in going from benzene to ethylbenzene are significantly different (Table 4): the activation energy of thermolysis decreases from 115 to 96–97 kJ mol⁻¹. The rate constants of peroxides thermolysis differ the most significantly at 50°C: **IIb** 0.35 s⁻¹ (benzene) and 0.69 s⁻¹ (ethylbenzene), **IIIb** 0.25 s⁻¹ (benzene) and 0.68 s⁻¹ (ethylbenzene). The increase in the rate constants of peroxydicarbonates thermolysis in passing from benzene to ethylbenzene (at 50°C) almost 2-fold (**IIb**) and 2.7-fold (**IIIb**) is due to the abstraction of a hydrogen atom from ethylbenzene by polyfluoroalkoxy radicals. The phenylethyl radicals formed in this case attack the peroxide groups of peroxydicarbonate:

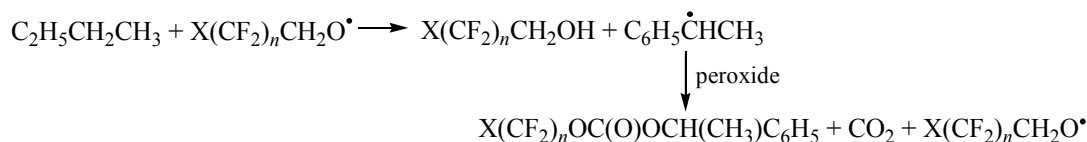
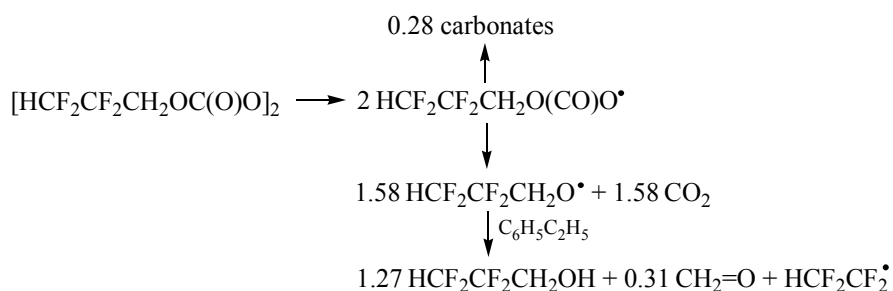


Table 4. Kinetic parameters of di(polyfluoroalkyl) peroxydicarbonates thermolysis ($4 \times 10^{-2} \text{ mol l}^{-1}$) in comparison with thermolysis of di(*n*-butyl) peroxydicarbonate **VII** ($1 \times 10^{-2} \text{ mol l}^{-1}$)

Peroxide	Solvent	Temperature, °C	$k \times 10^{-4}, \text{ s}^{-1}$	$\tau_{1/2}, \text{ min}$	$E_a, \text{ kJ mol}^{-1}$
IIb	Benzene	50	0.35 ± 0.04	320	115 ± 3
		60	1.20 ± 0.02	100	
		70	3.30 ± 0.02	35	
	Ethylbenzene	50	0.69 ± 0.04	183	96 ± 3
		60	1.96 ± 0.04	60	
		70	4.38 ± 0.02	28	
IIIb	Benzene	50	0.25 ± 0.06	462	115 ± 4
		60	1.00 ± 0.05	115	
		70	3.10 ± 0.02	38	
	Ethylbenzene	50	0.68 ± 0.03	172	97 ± 3
		60	1.90 ± 0.06	60	
		70	4.36 ± 0.04	28	
VI	Benzene	50	0.62 ± 0.05	186	113 ± 5
		60	2.20 ± 0.05	52	
		70	7.36 ± 0.04	16	

The formation of polyfluoroalkoxy radicals is confirmed by a high content of 1,1,3-trihydroperfluoropropanol (1.27 mol per 1 mol of peroxide), carbon

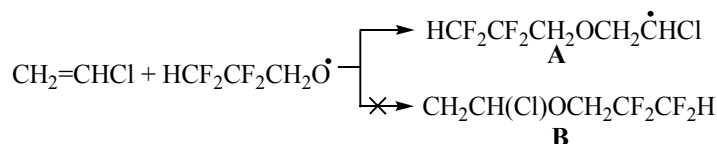
dioxide (1.58 mol per 1 mol of peroxide), and carbonate (0.28 mol per 1 mol of peroxide) in the thermolysis products of peroxide **IIb** in ethylbenzene at 70°C:



The carbonate radicals formed during the monomolecular decay of peroxydicarbonate **IIb** at the O–O bond transform into the tetrafluoropropoxy radicals and CO_2 (1.58 mol of CO_2 found per 1 mol of the decomposed peroxide). The main part of the tetrafluoropropoxy radicals (1.27 mol per 1 mol of the decomposed peroxide) reacts with ethylbenzene resulting in 1,1,3-trihydroperfluoropropanol (1.27 mol per 1 mol of the decomposed peroxide). A small part of these radicals (0.31 mol per 1 mol of the decomposed

peroxide) undergoes β -decay, which is consistent with the amount of the formaldehyde detected.

The electrophilic properties of polyfluoroalkoxy radicals generated from polyfluoroalkylperoxydicarbonate during polymerization of vinyl chloride facilitate the attack of the vinyl chloride H_2C group in comparison with the unsubstituted alkoxy radicals generated from dialkyl diperoxycarbonates. This reduces defects in the macromolecular chain of polyvinyl chloride [2] and results in its simultaneous nano-modification:



Radical **A** by 0.310 eV is more stable than **B**, which explains the preference of its formation. Therefore, the polyvinyl chloride suspension prepared using di(polyfluoroalkyl)peroxydicarbonates has a more ordered structure, contains less labile groups, and so is more thermally stable than in the case of the use of di(*n*-butyl) peroxydicarbonate [2].

EXPERIMENTAL

The ^1H NMR spectrum (CCl_4) was registered on a Varian Mercury instrument (300 MHz), internal reference HMDS. The IR spectra were recorded on a Specord-M82 instrument (from films).

Synthesis of di(1,1,3-trihydroperfluoropropyl)-peroxydicarbonate (IIb). Into a three-neck reactor equipped with a stirrer, thermometer, and dropping funnel were placed 33.0 g (0.25 mol) of 1,1,3-trihydroperfluoropropanol, 0.57 g (0.0078 mol) of *N,N*-dimethylformamide, and 8.14 g (0.15 mol) of liquid phosgene at -5 to 0°C . Then the temperature was raised to 90°C and 14.85 g (0.15 mol) of gaseous phosgene was passed through the reaction mixture for 2.5 h. As the reaction completed, hydrogen chloride and unreacted phosgene were removed from the reactor by blowing the dry nitrogen. The product was distilled at the reduced pressure to give 1,1,3-trihydroperfluoropropyl chloroformate **IIa**. Yield 45.2 g (93%).

To the cooled chloroformate **IIa** (45.2 g, 0.23 mol) was added sodium peroxide prepared from 17% aqueous solution of sodium hydroxide containing 9.2 g (0.23 mol) of NaOH, and 4.4 g of 30% hydrogen peroxide, at -5 to 0°C under vigorous stirring. The reaction mixture was stirred for 2 h with the gradual warming to 15 – 20°C . Then the organic layer was separated and washed with distilled water, dried with anhydrous sodium or magnesium sulfate, and kept at a reduced pressure for 30–40 min. Yield 31.7 g (78%). Peroxide **IIb** is a liquid with a characteristic odor. R_f 0.75 (silufol, acetone–diethyl ether–hexane, 0.5:1:1).

Yields, physicochemical constants of the synthesized polyfluoroalkyl chloroformates and di(polyfluoroalkyl) peroxydicarbonates are given Tables 2 and 3.

The kinetics of the di(polyfluoroalkyl) peroxydicarbonates thermolysis was studied in sealed tubes in benzene and ethylbenzene in the nitrogen atmosphere at 50, 60, and 70°C in an ultrathermostate. After a certain periods of time the tubes (1 ml) were taken out

(2 parallel samples), cooled and opened, and the amount of remaining peroxide was determined by the iodometric titration [1].

The composition of the thermolysis products of peroxydicarbonate in ethylbenzene solution was determined after keeping the samples at 70°C for at least 10 half-life periods in the ampules of 15 ml volume each. The gaseous products were analyzed on a Tsvet-104 chromatograph with a stainless steel column 300×0.4 cm, sorbent activated carbon AG-3. The column temperature 227°C , detector temperature 250°C , evaporator temperature 300°C . Carrier gas helium, pressure 25 kg cm^{-3} . The qualitative composition of the gases was determined by comparing the retention times of the pure samples and the reaction mixture components, the amount was determined by a simple normalization method.

Liquid products in the reaction mixture were identified and quantitatively determined on a Tsvet-134 chromatograph, column 300×0.4 cm, adsorbent SE-30 (5%) on Chromaton N-AW. The column temperature 60°C , detector temperature 110°C , evaporator temperature 270°C . Carrier gas helium, the rate $20 \text{ cm}^3 \text{ min}^{-1}$, the diagram sweep rate 600 mm h^{-1} . The identification of the liquid products was carried out by comparing the retention times of the pure samples, the reference substances in ethylbenzene and the components of the reaction mixture. The quantitative measurements were made using an internal reference method [8].

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