THE INFLUENCE OF DIMETHYLENEDIOXIDE GROUP IN POLYFLUOROALKYLPEROXYDICARBONATES ON DESTRUCTION PROCESS

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Abstract:*The influence of dimethylenedioxide groups on the destruction of di(OI-polyfluoroalkoxyethyl)peroxidecarbonates, $[H(CF_2)nCH_2OCH_2CH_2OC(O)O]_2$, here n= 2,4, in the absence of solvent or in benzene or ethylbenzene environment is shown.*

Keywords: *di(OI-polyfluoroalkoxyethyl)peroxide carbonates, dimethylenedioxide group, OI-polyfluoroalkoxyethylcarbonate radicals.*

It has been shown for peroxides [1-5] that polyfluorinated substituents provide considerable influence on their both induced and monomolecular decomposition. Among all carbonate peroxides a special place must be given to polyfluoroalkylperoxide carbonates, structural analogs of industrially applied di(OI-n-butoxyethyl)peroxy dicarbonate, that contain polyfluoroalkyl substituents instead of n-butoxy-group. Those peroxides differ from those studied earlier [6-9] by the presence of dimethylenedioxide groups in their structure.

Here we consider how induced (without solvent) or monomolecular decomposition of peroxide in benzene or ethylbenzene is influenced by a dimethylenedioxide group inserted between its polyfluoroalkyl fragment and peroxycarbonate group, the process is exemplified by the conversion of di(1,1,3-trihydroperfluoropropyl)peroxide carbonate $[HCF_2CF_2CH_2OC(O)O]_2$ (I) to di[2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethyl]peroxide carbonate, $[HCF_2CF_2 CH_2OCH_2CH_2OC(O)O]_2$ (III) and that of di(1,1,5-trihydroperfluoropentyl)peroxide carbonate $[H(CF_2CF_2)_2CH_2OC(O)O]_2$ (II) to di[2-(1Br',1Br',5Br'-trihydroperfluoropentoxy)ethyl]peroxide carbonate, $H(CF_2CF_2)_2 CH_2OCH_2CH_2OC(O)O]_2$ (IV).

Peroxide carbonates III, IV were prepared from industrially produced alcohol-telomeres (moreover, 1,1,5- trihydroperfluoropentanol (V) is a waste from the manufacture of 1,1,3-trihydro perfluoropropanol (VI) [3]): under the action of ethylene chlorohydrin in alkaline medium 2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethanol, $HCF_2CF_2 CH_2OCH_2CH_2OH$ (VII), and 2(1Br',1Br',5Br'-trihydroperfluoropentoxy)ethanol, $[H(CF_2CF_2)_2CH_2OCH_2CH_2OH$ (VIII) were synthesized [6, 10], then alcohols VII and VIII in liquid phosgene medium were converted to related chloroformates and further, under the action of sodium peroxide those chloroformates were converted to peroxide carbonates I вЂ" IV with yield 78-86% (Table1) [7,8].

Table 1*. Yield and properties of polyfluoroalkyl- and OIвЂ"(polyfluoroalkoxy)ethyl peroxide carbonates*

Peroxide	Yield, %	n^{20}_D	d^{20}_4
I	78	1.3548	1.6214
II	80	1.3362	1.7167
III	86	1.3828	1.4952

	IV	85	1.3630	1.6138

B

We investigated the stability of polyfluorinated peroxide carbonates in the absence of solvents that is most important for peroxide storage and handling. It was found that the stability of polyfluorinated peroxide carbonates exceeds considerably that of di(OI-n-butoxyethyl) peroxide carbonate, [n-$C_4H_9OCH_2CH_2OC(O)O]_2$, (IX) (Table 2) widely applied in industry. For peroxide II after 180 days of storage at +5B°C no decomposition was mentioned, however, for the same peroxide heated in benzene to 50B°C its half-decomposition period was 7.7 hours (Table 2). When changing from peroxide II to peroxide I the length of the perfluorinated chain decreases, and the degree of decomposition goes up slightly (up to 1%). The introduction of dimethylenedioxide chain between polyfluoroalkyl fragment and peroxycarbonate group in peroxidecarbonate I, when changing to peroxidecarbonate III decreases the peroxide stability during storage: the degree of its decomposition after 180 days storage increases up to 3%, while the period of its half-decomposition decreases by 39% when the peroxide is heated at 50B°C in benzene. From the comparison one may see that peroxidecarbonate III is much more stable than di(OI-n-butoxy)ethylperoxide carbonate that when stored at 0B°C decomposed during 8 days by 8%, and at 50B°C in benzene its half-decomposition period is 1.1 hour only.

Table 2. The impact of peroxide structure and dimethylenedioxide group introduction on their stability at storage

Peroxide	Stability at storage			Period of half-decomposition at 50B°C, (benzene), hours
	Temperature of storage, B°C	Time of storage, days	Degree of decomposition, %	
I	5	180	1	5.3
II	5	180	0	7.7
III	0-5	180	3	4.8
IX	0	8	8	1.1

The results of our study on the stability of peroxides stored at 0-5B°C reflect mainly the ability of peroxides to undergo induced decomposition. This necessitated investigation of thermal decomposition of polyfluoroalkylperoxide carbonates in organic solvents, e.g. benzene or ethylbenzene, at the minimal possible concentration of peroxide, so that its further decrease would not influence on the rate of the peroxide thermolysis (the peroxide initial concentration no more than $(4-5)B \cdot 10^{-2}$ mole/l), and under those conditions monomolecular decomposition of peroxide usually takes place.

The influence of dimethylenedioxide group on the rate constant of polyfluoroalkylperoxide carbonates I or II thermal decomposition is shown in **Table 3** (thermal decomposition of those two peroxides in benzene and ethylbenzene was reported by us earlier [9]). The introduction of a dimethylenedioxide group into peroxide I results in higher rate of peroxide III monomolecular decomposition by O-O bond in benzene by 29-30% (at 50 or 60B°C) or by 38% (at 70B°C). The effect of dimethylenedioxide group on the rate of monomolecular decomposition for peroxide with longer perfluorinated chain (peroxide IV) is somewhat larger than that for peroxide III, it totals: 29.5% - 37.5% (50, 60B°C) and 40%(70B°C).

Thermal decomposition of peroxides I- IV in ethylbenzene differs considerably from that in benzene: the rate constant of monomolecular decomposition for peroxides without dimethylenedioxide group (I, II) are nearly the same, their value being about $kB \cdot 10^{-4}$, c^{-1}: 0.68-0.69 (50B°C), 1.90-1.96 (60B°C), 4.36-4.38 (70B°C). For peroxides III and IV containing dimethylenedioxide groups the rate of their thermolysis in ethylbenzene is less than that of peroxides I and II. The thermolysis rate constants for peroxides III and IV are virtually the same at 50 and 60B°C, their values being ($kB \cdot 10^{-4}$, c^{-1}): 0.36-0.39 (50B°C), 1.08(60B°C). This evidences for negligible impact of the length of perfluorinated chain on the said thermolysis process, determined chiefly by the presence of dimethylenedioxide group.

The results are explicable on the basis of difference between those peroxide thermal decomposition mechanism and the properties of radicals formed therewith. Peroxides I and II perform as the sources of polyfluoroalkoxy radicals resulting from OI-decomposition of carbonate radicals.

Polyfluoroalkoxy radicals split hydrogen of CH_2-group in ethylbenzene, and thus formed O±-phenylethyl radicals participate in induced decomposition of the original peroxide [9].

The revealed by us impact of dimethylenedioxide groups on the decrease of monomolecular decomposition rate constant in ethylbenzene for polyfluoroalkylperoxy dicarbonates III and IV is explained by the properties of carbonate radicals with dimethylenedioxide groups, resulting from the decomposition of those peroxides. Those carbonate radicals do not tend to split-off hydrogen from CH_2-group in ethylbenzene, but undergo cycling or condensation reactions the same manner as OI-(acyloxy)ethylcarbonate radicals formed due to the thermolysis of OI-(acyloxy)ethylperoxide carbonates [6] resulting in the formation of A-C substances as follows:

$$[RCOOCH_2CH_2\text{-O-C-(O)-O-}]_2$$
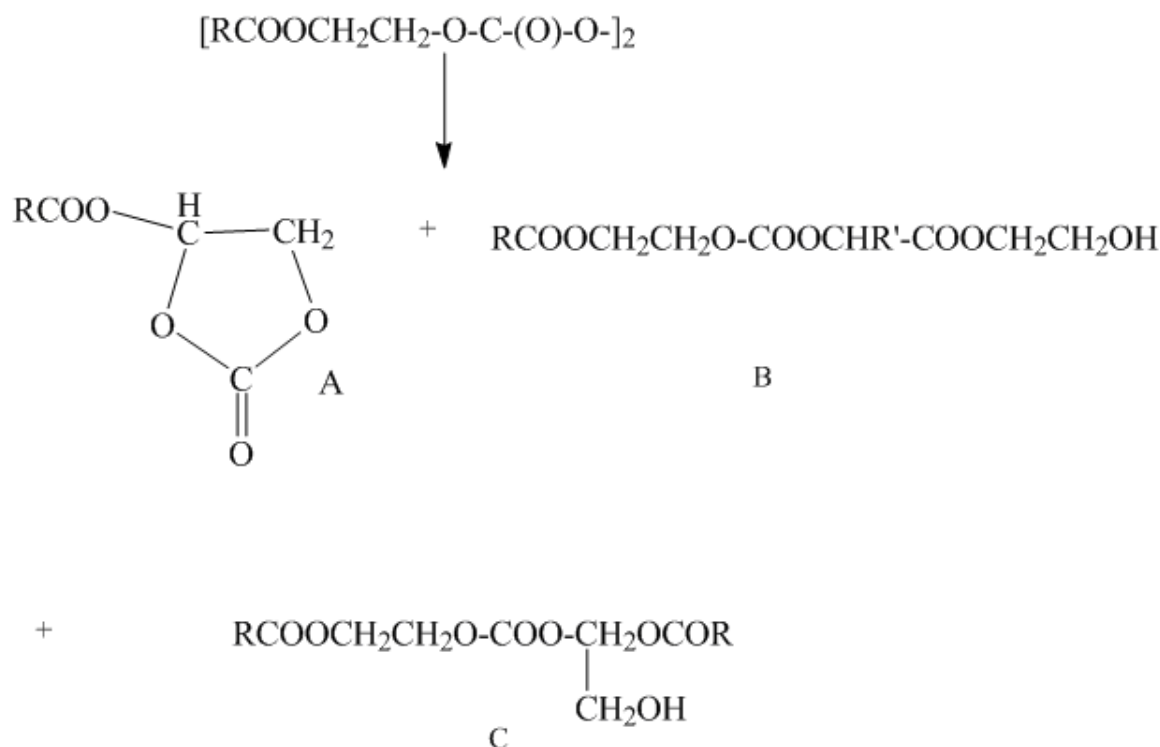
Considerable drop in the rate of thermolysis in ethylbenzene for peroxides III and IV, unlike peroxides I and II, points to small probability of participation in chain-radical reactions for peroxidecarbonate radicals with dimethylenedioxide groups originally formed during the decomposition process.

For peroxides III and IV when changing from ethylbenzene to benzene it should be marked that their thermolysis rate constant in benzene exceeds much that in ethylbenzene. This kind of solvent effect on the thermolysis is explicable by the difference in electronic density distribution within those hydrocarbons and in their interaction with fluorines belonging to the perfluorinated chain of the peroxide molecule. The nature of those interactions was considered elsewhere [11, 12]. Therefore, heat of adsorption (q, kJ) for aromatic hydrocarbons and perfluoroalkyl groups are 33.4 for benzene and 43.5 for ethylbenzene. Standard entropy values (-O"S J/mole Pљ) for the said hydrocarbons and CF_3- group are 120 for benzene and 135 for ethylbenzene. Probably, during the process of monomolecular decomposition of peroxide carbonates by their O-O bond within the solvent B«cageB» thermolysis is considerably influenced by the solvent adsorbability and polarity that determine the formation of B«cageB» structure.

EXPERIMENTAL

PMR spectra were recorded by Varian Mercury 300 MHz. HMDS was applied for the internal standard. CCl_4, $CDCl_4$ were used for solvents.

IR spectra were recorded by B«Specord вЋ" M82B» in thin layer (liquid film).

In PMR spectra of all synthesized peroxide carbonates the signal of end-proton in HCF_2-group is a triplet of triplets with the centre at 5.8B±0.05 ppm with spin-spin interaction constant of O±-atoms J_{H-F}=52 Hz, each of its components being split into a triplet with spin-spin interaction constant of OI-fluorines J_{H-F}=5.5 Hz.

The signal of two protons in $-CF_2-CH_2$-group is observed in the form of well-resolved triplet at 4.6B±0.03 ppm with spin-spin interaction constant J_{H-F}=5.5Hz.

In IR spectra di(polyfluoroalkyl)peroxidecarbonate in the area of >C=O group stretch vibrations two bands at 1778B±2 and 1807B±3 cm^{-1} are observed that correspond to carbonyl group stretch vibrations in non-substituted peroxide carbonates [1, 3, 8]. This evidences that polyfluoroalkyl groups in OI-positions to peroxide carbonate group do not have considerable influence on the molecule spectral

characteristics. The stretch vibrations of OвЂ"O bond in di(polyfluoroalkyl)peroxide carbonates are observed at 845вЂ"850 cm^{-1}. Those of peroxide chain CвЂ"OвЂ"OвЂ"C are observed at 1041вЂ"1094 cm^{-1}, the fact is in agreement with published data [3, 8].

Di[2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethyl]peroxide carbonate, [HCF$_2$CF$_2$ CH$_2$OCH$_2$CH$_2$OC(O)O]$_2$ (III)

A. Synthesis of 2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethanol, HCF$_2$CF$_2$ CH$_2$OCH$_2$CH$_2$OH

A reactor is charged with 4.5g (0.11mole) of 70% aqueous solution of sodium hydroxide and consequently 9.15g (0.11mole) of 1.1.3-trihydroperfluoropropanol and 9.15g (0.11mole) of ethylenechlorohydrin are added. The reaction mass is heated to 70B°C and stir for 4 hours. The solution is then dried with sodium sulphate and distilled under vacuum. The yield of 2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethanol is 73%, its $T_{boiling}$ is 50B°C/1mm, n^{20}_D 1.3613, d^{20}_4 is 1.3678 (2-(1Br',1Br',5Br'-trihydroperfluoropentoxy)ethanol was produced in the same manner with yield 71%, its $T_{boiling}$ is 58-60B°C/1mm, n^{20}_D1.3469, d^{20}_4 1.5500), the fact is in agreement with published data [10].

B. Synthesis of 2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethylchloroformate, HCF$_2$CF$_2$ CH$_2$OCH$_2$CH$_2$OC(O)Cl

Phosgene treatment of 2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethanol is conducted following the common procedure [7, 8, 10]. The yield of chloroformate is 93%, its $T_{boiling}$ is56-57B°C/1mm, n^{20}_D1.3821, d^{20}_4 14420 (2-(1Br',1Br',5Br'-trihydroperfluoropentoxy)chloroformate was produced in the same manner with yield 78%, its $T_{boiling}$ is 70B°C/1mm, n^{20}_D 1.3656, d^{20}_4 1.5793).

C. Synthesis of 2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethylperoxide carbonate, [HCF$_2$CF$_2$ CH$_2$OCH$_2$CH$_2$OC(O)O]$_2$

A three-necked reactor equipped with a stirrer, thermometer and drop-funnel is charged with 2.25g (0.056 moles) of sodium hydroxide as 17% aqueous solution at 0B°C, 2.0g of 45% sodium peroxide solution is added. The reaction mass is mixed at the said temperature for 20min., and then solution 13.07g (0.056 mole) of 2-(1Br',1Br',3Br'-trihydroperfluoropropoxy)ethyl chloroformate dissolved in 15ml of absolute diethyl ether is dropwise added into the reactor. The reaction mass temperature is increased to 10B°C, and stirred for 2 hours. Then it is stirred 1 hour more at 20B°C. Organic layer is separated and washed with water to pH =6, dried with waterless sodium sulphate, separated, after that solvent and impurities are separated under vacuum (1mm Hg) during 40 min. at 20B°C. The yield was 86%, n^{20}_D 1.3828, d^{20}_4 1.4952 (2-(1Br',1Br',5Br'-trihydroperfluoropentoxy) ethylperoxide carbonate was produced in the same manner with yield 85%, , n^{20}_D 1.3630, d^{20}_4 1.6138).

Kinetics of the thermal decomposition of di(polyfluoroalkyl)peroxy dicarbonates was studied using ampoule method in benzene and ethylbenzene in clean nitrogen environment at 50, 60, and 70B°C in an ultrathermostate. Ampoules (volume 1ml) are taken out in designed time periods (2 parallel samples), cooled, and opened, and the amount of non-destructed peroxide is determined by the iodometric titration method [6].

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