3-Tert-butyl-5-butylthio-2-methoxy-Δ^4-1,3,2-oxazaphospholine (IIIa). A sample of 8.5 ml dry Et_3N was added gradually with stirring to a solution of the hydrochloride salt of ester (Ia) in 100 ml anhydrous chloroform at −10°C in a dry argon atmosphere. Then, a solution of 2.55 g methyl dichlorophosphite in 10 ml $CHCl_3$ was added slowly. On the following day, the IR band for the CO group had disappeared and the solvent was distilled off at atmospheric pressure. The mixture was diluted with absolute ether, filtered, and distilled to give oxazaphospholine (IIIa) in 53% yield, bp 88°C (0.01 mm Hg), n_D^{20} 1.5540. Found: P, 11.58; N, 5.47; S, 12.37%. Calculated for $C_{11}H_{23}NO_2PS$: P, 11.76; N, 5.32; S, 12.18%. IR spectrum in CCl_4 (ν, cm^{-1}): 1605 (C=C), 3115 (−CH=). PMR spectrum (δ, ppm, J, Hz): 0.8 t (3H, $\underline{CH_3}CH_2$, $^3J_{HH}$ = 7.2), 1.3 d (9H, t-Bu, $^4J_{HP}$ = 1.2), 1.5 m (4H, CH_2CH_2), 2.54 m (2H, SCH_2), 3.15 d (3H, CH_3O, $^3J_{HP}$ = 7.8), 6.33 d (1H, −CH=, $^3J_{HP}$ = 5.6). δ_P = 126.8 ppm.

3-Tert-butyl-5-butylthio-2-oxo-Δ^4-1,3,2-λ^5-oxazaphospholine (IIIb). Oxazaphospholine (IIIb) was obtained under the conditions described in 50% yield, bp 125°C (0.01 mm Hg), mp 52-53°C (from decane). Found: P, 12.02; N, 5.33; S, 12.42%. Calculated for $C_{11}H_{22}NO_2PS$: P, 11.76; N, 5.32; S, 12.18%. IR spectrum in KBr pellet (ν, cm^{-1}): 1243, 1270 (P=O), 1615 (C=C), 3080 (−CH=). PMR spectrum in CD_2Cl_2 (δ, ppm, J, Hz): 0.88 t (3H, CH_3CH_2, $^3J_{HH}$ = 7.3), 1.38 s (9H, t-Bu), 1.53 m (4H, CH_2CH_2), 1.74 d (3H, CH_3P, $^2J_{HP}$ = 16.9), 2.59 t (2H, SCH_2, $^3J_{HH}$ = 7.4), 6.4 d (1H, −CH=, $^3J_{HP}$ = 22), δ_P = 43.2 ppm.

LITERATURE CITED

1. Yu. G. Gololobov and Yu. V. Balitskii, Zh. Obshch. Khim., **44**, No. 10, 2356 (1974).
2. Yu. G. Gololobov and L. I. Nesterova, Zh. Org. Khim., **14**, No. 4, 739-745 (1978).
3. Yu. G. Gololobov and L. I. Kruglik, Zh. Org. Khim., **17**, No. 4, 869 (1981).

THERMAL DECOMPOSITION OF PEROXIDE DERIVATIVES OF POLYFLUORINATED β-KETOESTERS

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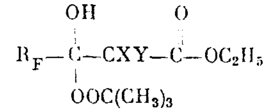
The thermal flow microcalorimetric method was used to determine the kinetic parameters for the thermal decomposition of peroxide derivatives of polyfluorinated β-ketoesters and the decomposition products were established.

Polyfluorinated peroxides have not been studied extensively [1,2] although these compounds hold considerable interest for the polymerization of fluoromonomers or the structurization of fluororubbers since the use of nonfluorinated peroxide initiators leads to deterioration of thermal and chemical stability of polymer materials [3,4]. Since peroxide derivatives of polyfluorinated β-ketoesters may be efficient initiators and modifiers in the polymerization of vinyl monomers, it was of interest to study the kinetics and mechanism of their thermal decomposition. There is presently no information available on the thermolysis of peroxides derived from polyfluorinated β-ketoesters.

In this work, we studied compounds with the general formula



$$R_F-\overset{\overset{OH}{|}}{\underset{\underset{OOC(CH_3)_3}{|}}{C}}-CXY-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

(Ia-e)

$X = Y = H$, $R_F = CF_3$ (a), $H(CF_2)_2$ (b), $H(CF_2)_4$ (c); $X = H$, $Y = Cl$, $R_F = H(CF_2)_4$ (d); $X = Y = Br$, $R_F = H(CF_2)_4$ (e).

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TABLE 1. Kinetic Parameters of the Thermal Decomposition of Polyfluorinated Hydroxyperoxides (Ia)-(Ie)

Compound	T, °C	$K \cdot 10^3$, $\sec^{-1}$	E, kcal/mole
(Ia)	70	0,67	29,67
	80	2,01	
	90	6,05	
(Ib)	70	0,47	33,4
	80	1,81	
	90	6,61	
	100	33,70	
(Ic)	80	0,73	30.1
	90	2,40	
	100	6,92	
(Id)	70	0,47	29,4
	80	1,51	
	90	4,50	
(Ie)	70	0,88	23,3
	80	4,57	
	90	5,24	
	100	12,62	

The thermal decomposition of hydroxyperoxides has been studied by the thermal flow microcalorimetric method [5].

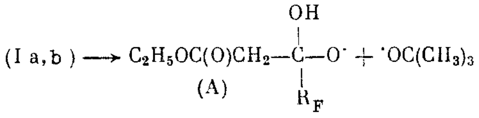
Table 1 gives the rate constants for the thermal decomposition and activation parameters for the reaction obtained by standard procedures [6].

The results of this study indicate decreasing thermolysis rate with increasing length of the fluoroalkyl substituent. Thus, the rate of thermal decomposition of (Ia) at 80°C is 2.7 times greater than for (Ic). The lower rate for the decomposition of peroxide (Ib) in comparison with (Ia) is attributed to existence of a cyclic isomer formed by the reaction of the terminal proton of the fluoroalkyl substituent with an oxygen atom of the peroxide group, which is also indicated by the ^{19}F NMR spectrum. Thus, the quartet at δ 46.7 ppm, J = 286 Hz corresponds to the HCF_2 group [7].

The introduction of halogen atoms into the α-methylene group of peroxides (Id) and (Ie) leads to an increase in the rate of decomposition of the peroxides in comparison with (Ia)-(Ic).

In order to determine the direction of the thermal decomposition of peroxide derivatives of polyfluorinated β-ketoesters (Ia) and (Ib), we studied the products of the decomposition of the peroxides (Table 2).

These data indicate the possibility of an initial homolytic dissociation of the O-O bond.



$$(\text{I a,b}) \longrightarrow \underset{(\text{A})}{C_2H_5OC(O)CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R_F}{|}}{C}}-O^{\cdot}} + {}^{\cdot}OC(CH_3)_3$$

The tert-butoxy radical undergoes decomposition to give acetone (44-60%) and reacts with the substrate (39-45%) to give tert-butyl alcohol.

The α-hydroxyalkoxy radical has a more complex fate. A significant amount of trifluoroacetic acid (0.61 mole) formed in the decomposition of (Ib) indicates the possibility of β-decomposition proceeding in a solvent cage.

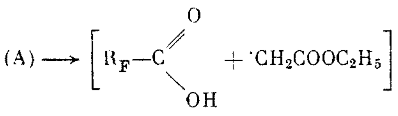
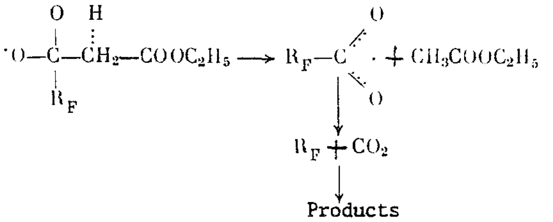


TABLE 2. Composition of the Products of the Decomposition of Peroxides (Ia) and (Ib) (mole per mole peroxide)

Decomposition product	(Ia)	(Ib)	Decomposition product	(Ia)	(Ib)
CF_3COOH	0,61	–	$(CH_3)_3COH$	0,39	0,45
HCF_2CF_2COOH	–	0.21	CH_3COCH_3	0,6	0,44
$CF_3COOC_2H_5$	0.25	–	C_2H_5OH	0,05	0,16
$HCF_2CF_2COOC_2H_5$	–	0.61	CO_2	0.19	0.21
$CH_3COOC_2H_5$	0,70	0,23			

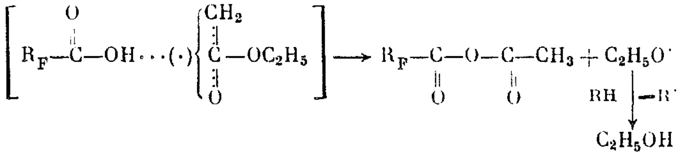
Ethylcarboxymethyl radicals react within and outside the cage to give 0.23-0.70 mole ethyl acetate. The formation of the hydroxyacyl radical due to the decomposition of (A) through a radical transition state is not excluded.



$$\cdot O-\overset{\overset{O\cdots H}{|}}{\underset{\underset{R_F}{|}}{C}}-CH_2-COOC_2H_5 \longrightarrow R_F-C\overset{O}{\underset{O}{\lessgtr}}\cdot + \cdot CH_2COOC_2H_5;\quad R_F-CO_2\cdot \rightarrow R_F + CO_2 \rightarrow \text{Products}$$

The formation of a significant amount of CO_2 (0.19-0.21 mole) indicates the possible participation of acetoxy radicals in the decomposition.

We may also propose the generation of the ethoxy radical according to the following scheme:



$$\left[R_F-\overset{O}{\overset{\|}{C}}-OH\cdots(\cdot)\begin{Bmatrix}CH_2\\ \vdots\\ C-OC_2H_5\\ \vdots\\ O\end{Bmatrix}\right] \longrightarrow R_F-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3 + C_2H_5O\cdot \xrightarrow[-R\cdot]{RH} C_2H_5OH$$

The content of 0.05-0.16 mole ethanol in the decomposition products supports this hypothesis.

It is difficult to derive a final conclusion concerning the nature of the homolytic transformations in light of the contribution of heterolytic peroxide decomposition reactions by the action of the strong fluorocarboxylic acids formed and due to secondary reactions involving the decomposition products.

EXPERIMENTAL

The products of the peroxide decomposition products were analyzed on an LKhM-8MD chromatograph with a flame ionization detector on a 3 m × 3 mm column packed with 10% Apiezon on Chromaton N-AW-DMCS. The nitrogen gas carrier flow rate was 40 ml/min. Solutions of 0.2 mole/liter peroxide in chlorobenzene solution were placed in ampuls and flushed with argon. The ampuls were sealed and decomposition was carried out. The ^1H and ^{19}F NMR spectra were taken on a Tesla BS-567A spectrometer in $CDCl_3$ with HMDS as the internal standard and CF_3CO_2H as the external standard, respectively.

Peroxides (Ia)-(Ie) were described in our previous work [8]. The starting polyfluorinated β-ketoesters were obtained according to our previous procedure [9].

Peroxides (Ia) and (Ic)-(Ie) are colorless liquids at -20°C, while (Ib) exists as colorless needle crystals. (Ia), n_D^{20} 1.392. PMR spectrum (δ, ppm): 1.20 s [9H, $(CH_3)_3$], 1.22 s (3H, CH_3), 2.82 q (2H, CH_2, J = 4 Hz), 4.22 q (2H, OCH_2, J = 5 Hz), 7.06 s (1H, OH).

(Ib), mp 31-32°C. PMR spectrum (δ, ppm, J, Hz): 1.17 s [9H, $(CH_3)_3$], 1.26 s (3H, CH_3), 2.83 q (2H, CH_2, J = 3), 4.20 q (2H, OCH_2, J = 8), 6.10 t.t (1H, $H(CF_2)_2$, $J_{H\text{-}CF_2}$ = 54, $J_{H\text{-}CF_2CF_2}$ = 6), 7.02 s (1H, OH).

(Ic), n_D^{20} 1.380. PMR spectrum (δ, ppm, J, Hz): 1.20 s [9H, $(CH_3)_3$], 1.22 s (3H, CH_3), 2.91 q (2H, CH_2, J = 10), 4.24 q (2H, OCH_2, J = 8), 6.15 t.t (1H, $H(CF_2)_4$, $J_{H\text{-}CF_2}$ = 54, $J_{H\text{-}CF_2CF_2}$ = 7), 6.86 s (1H, OH).

(Id), n_D^{20} 1.392. PMR spectrum (δ, ppm, J, Hz): 1.16 s [9H, $(CH_3)_3$], 1.19 s (3H, CH_3) 4.20 q (2H, OCH_2, J = 8), 5.42 s (1H, CH), 6.05 t.t [1H, $H(CF_2)_4$), $J_{H\text{-}CF_2} = 52$, $J_{H\text{-}CF_2CF_2} = 6$), 7.12 s (1H, OH).

(Ie), n_D^{20} 1.4040. PMR spectrum (δ, ppm, J, Hz): 1.14 s (9H, $(CH_3)_3$), 1.19 s (3H, CH_3), 4.25 q (2H, OCH_2, J = 7), 6.10 t.t (1H, $H(CF_2)_4$, $J_{H\text{-}CF_2} = 51$, $J_{H\text{-}CF_2CF_2} = 6$), 7.22 s (1H, OH).

The purity of the peroxides was determined using thin-layer chromatography, NMR spectroscopy, and analysis for active oxygen. The purity of the peroxide samples studied was at least 98.5%.

Analytical-grade chlorobenzene was subjected to additional purification according to Reichhard [10].

The kinetic measurements were carried out on a Calvet diathermic microcalorimeter with TBO semiconductor thermal flow sensors with 0.25 V/W sensitivity [6]. The thermal decomposition of the peroxides was carried out in a 7-ml glass microreactor placed in a calorimetric cell. A solution of the corresponding peroxide in chlorobenzene was first flushed with argon. The peroxide concentration did not exceed 0.01 mole/liter, which virtually excluded the possibility of induced decomposition. An analogous reactor with chlorobenzene was placed in the reference cell. The intensity of the heat evolution was calculated using the algorithm described in our prevoius work [6]. The linear dependence $\ln W = A(\tau)$ was used to calculate the rate constants in accord with the first-order thermokinetic equation for nonequilibrium reactions $\ln W = a - b\tau$. In this equation, a and b are related with the heat effect and rate constant by the equations

$$-\Delta H = (\exp a)/K$$
$$K = b.$$

LITERATURE CITED

1. R. A. De Marco and M. Shreeve, J. Inorg. Chem. Radiochem., 16, 109 (1974).
2. Z. R. Anderson, C. T. Ratcliffe, D. E. Jong, and W. B. Fox, J. Fluor. Chem., 7, 481 (1976).
3. L. Wall, Fluoropolymers [Russian translation], Mir, Moscow (1975), p. 248.
4. S. P. Novitskaya, Z. N. Nudel'man, and A. A. Dontsov, Fluoroelastomers [in Russian], Khimiya, Moscow (1988), p. 70.
5. E. Calvet and A. Prat, Microcalorimetry [Russian translation], Izd. Inos. Lit., Moscow (1963), p. 477.
6. B. I. Panfilov, A. I. Val'dman, A. P. Khardin, et al., Izv. Akad. Nauk LatvSSR, No. 3, 341 (1983).
7. J. Emsley, J. Finney, and L. Sutcliffe, High-Resolution NMR Spectroscopy [Russian translation], Vol. 2, Mir, Moscow (1968), p. 240.
8. V. V. Chapurkin, E. M. Volyskaya, and S. L. Kokorin, Organic Peroxides and Their Homolytic Reactions [in Russian], Izd. Volgogradsk. Ped. Inst., Volgograd (1987), p. 28.
9. V. I. Saloutin, Z. É. Skryabina, M. N. Rudaya, and K. I. Pashkevich, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1106 (1984).
10. H. Reichhard, Solvents in Organic Chemistry [Russian translation], Khimiya, Leningrad (1973), p. 150.