ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 2, pp. 242–245. © Pleiades Publishing, Ltd., 2009.
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Synthesis and Features of Thermolysis of Fluorine-containing Aromatic 1-Hydroxy-1-hydroperoxides and 1,1'-Dihydroperoxides

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Received May 15, 2008

Abstract—Aromatic fluorine-containing 1-hydroxy-1-hydroperoxides and 1,1'-dihydroxyperoxides were obtained and their thermolysis features were studied. The fluorine atoms incorporation into the aromatic ring of 1-hydroxy-1-hydroperoxides was found to lead to their thermal stability increase. 1,1'-Dihydroxyperoxides are the less thermal stable than 1-hydroxy-1-hydroperoxides. Compared to the fluorine atoms, incorporation of fluoroalkyl groups into the aromatic ring exerts greater effect on the stability of the peroxide.

DOI: 10.1134/S1070363209020121

Homolysis yielding free radicals is the most important reaction of peroxide compounds. Peroxide thermolysis studying allows regularities of influence of structure on their reactivity to be established that is of great importance to detection of possible practical use of peroxide compounds as initiators for free-radical processes [1]. Reactivity of the both peroxides and the generated free radicals is determined by their electronic structure and depends considerably on the reaction medium and temperature conditions. Study of the character of peroxide with solvent interaction, thermolysis and decay products composition allows to establish the reaction mechanism, to estimate a possibility of peroxides use in various technological processes and to select optimal temperature condition.

Thermolysis of the fluorinated organic peroxide derivatives of carbonyl compounds is not virtually examined. It is known [2] that dihydroperoxides on the matrix of the fluorinated aliphatic ketones are the less flammable and shock and friction sensitive than their unsubstituted analogs. But they are the less stable than hydroperoxides, into which they are transforming for one day at 25°C.

In the present work the synthesis of fluorine-containing aryl-1-hydroxy-1-hydroperoxides **Ia–Id** by the reaction of benzaldehyde and its fluorine-substituted analogues with hydrogen peroxide is given.

$$\text{Ar–CH=O + HOOH} \rightarrow \underset{\textbf{Ia–Id}}{\text{Ar–CH(OH)–OOH}},$$

Ar = C_6H_5 (**a**), *p*-FC_6H_4 (**b**), C_6F_5 (**c**), *o*-$CF_3C_6H_4$ (**d**).

Reaction was carried out at –25 to –20°C in tetrachloromethane solution distilled previously over P_2O_5. 70–98% Hydrogen peroxide was used.

Thermolysis of the fluorine-containing aryl-1-hydroxy-1-hydroperoxides **Ia–Ic** prepared proceeds in chlorobenzene at the initial concentration of hydroxyhydroperoxide of 0.01–0.02 mol l^{-1} in the temperature range of 323–373 K. Thermolysis at the initial time point was established to be described satisfactorily with the first-order equation. Kinetics studying results are given in Table 1.

The data obtained show that the thermal stability of aromatic hydroxyperoxides increases, when the fluorine atoms are incorporated into the peroxide molecule. The presence of the five fluorine atoms in the ring leads to increase thermolysis activation energy by 38 kJ mol^{-1} in comparison with the unsubstituted compound. This rise is due to the strong electronegative inductive effect of the fluorine atoms decreasing electron density on the oxygen atoms of the peroxide bond. The latter results in hydroxyhydroperoxides thermal stability growth.

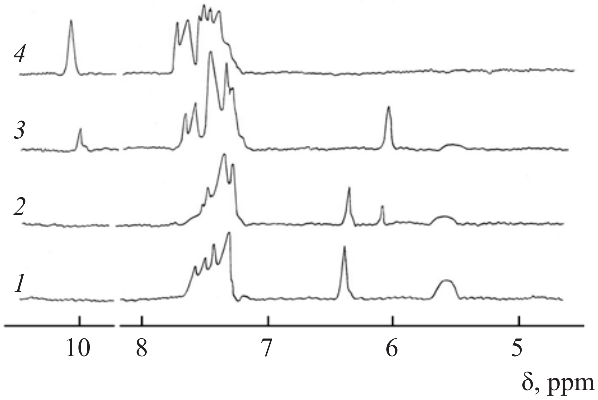

Fig. 1. The ^{1}H NMR spectra of peroxide $[C_6H_5–CH(OH)–O]_2$ at 60°C, τ, min: (*1*) 0, (*2*) 3, (*3*) 7, and (*4*) 15.

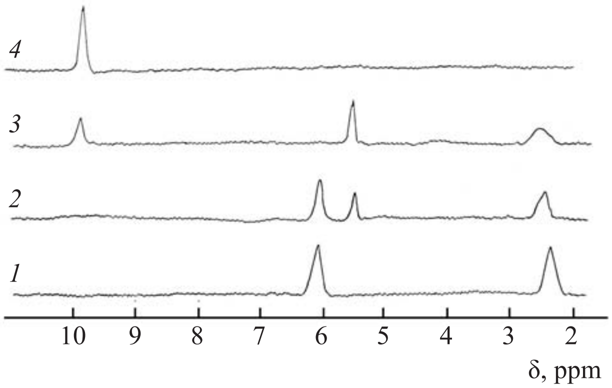

Fig. 2. The ^{1}H NMR spectra of peroxide $[C_6F_5–CH(OH)–O]_2$ at 90°C, τ, min: (*1*) 0, (*2*) 2, (*3*) 4, and (*4*) 20.

The fluorine-containing aryl-1,1'-dihydrohydroxyperoxides were prepared by the reaction of benzaldehyde and its fluorine-substituted analogues with 30% hydrogen peroxide.

$$2\ Ar–CH{=}O + HOOH \rightarrow Ar–CH(OH)–OO–CH(OH)–Ar,$$

IIa–IId

Ar = C_6H_5 (**a**), *p*-F-C_6H_4 (**b**), C_6F_5 (**c**), *o*-$CF_3C_6H_4$ (**d**).

Reaction was carried out using fivefold excess of hydrogen peroxide. The excess decreasing leads to a drop in the target product yield. Yield of peroxides achieves 74–98%.

Thermolysis of aryl-1,1'-dihydroxyperoxides **IIa–IId** was found to proceed through a stage of hydroxylhydroperoxide formation. Therefore iodometric method was unusable. Thermolysis of the fluorine-containing aryl-1,1'-dihydrohydroxyperoxides **IIa-IId** was exmined employing the ^{1}H NMR spectroscopy.

Thermolysis was carried out in acetonitrile since dihydroxyperoxides are insoluble in the other nonpolar solvents such as chlorobenzene, ethylbenzene and cumene. Variations with time in the ^{1}H NMR spectra of peroxides **IIa** and **IIb** occurring at their thermolysis are shown on Figs. 1 and 2.

In the ^{1}H NMR spectrum of **IIa** the signals of OH- (5.45 ppm) and CH-moieties (6.31 ppm) decrease at 60°C. Within 3 min a new signal at δ 6.03 ppm appears. After 7 min the signal of CH (6.31 ppm) disappears fully. Intensity of the signal at δ 6.03 ppm increases and a new signal at δ 10.01 appears. Within 15 min the signal at δ 6.03 disappears, but intensity of the signal at δ 10.01 ppm grows and does not change during 20–30 min.

In the studies of the ^{1}H NMR spectra of starting benzal-dehyde, benzoic acid and 1-hydroxy-1-hydroperoxide **Ia** the signal at 6.03 ppm was found to correspond to CH-group of **Ia** and the signal at δ 10.01 ppm belongs to CH-moiety of initial benzaldehyde.

There are two signals at 2.48 ppm (OH) and 6.56 ppm (CH) in the ^{1}H NMR spectrum of **IIc**. Within 2 min intensities of these signals decrease and a new signal at δ 6.30 appears. After 4 min the CH signal (6.56 ppm) disappears; the signal at δ 6.30 grows and a new signal at δ 10.17 ppm appears. After 20 min of thermolysis of **IIc** in acetonitrile at 90ºC only one signal at δ 10.17 ppm is observed in the spectrum. Intensity of the latter does not change during 30–60 min. Analysis of the ^{1}H NMR spectra of pentafluorobenzaldehyde, pentafluorobenzoic acid and 1-hydroxy-1-hydroperoxide **Ic** showed that the signal at 6.30 ppm belongs to CH-moiety of **Ic**, and the signal at δ 10.17 ppm corresponds to CH-moiety of pentafluorobenzaldehyde.

Table 1. Rate constants of thermolysis and activation energies of fluorine-containing aralkyl-1-hydroxy-1-hydroperoxides

Compound	*T*, °C	$\kappa\times10^5$, s^{-1}	*E*, kJ mol^{-1}
Ia	60	0.69	122.5
	70	2.55	
	75	4.43	
Ib	50	0.34	129.2
	60	1.39	
	70	5.69	
Ic	80	0.41	160.9
	90	1.83	
	100	7.65	

Thermolysis of compounds **IIa-IId** was carried out in the temperature range of 313–363 K using initial concentration of peroxide 0.05–0.1 mol l^{-1}. The found rate constants of thermolysis and activation energies are given in Table 2.

Data obtained show that essential growth of the heat stability of peroxides studied is observed, when trifluoromethyl group is incorporated (compound **IId**). The rate constants of thermolysis of **IId** at 70°C is 6–7 times lower than for compounds **IIb** and **IIc**. The absence of electron-accepting effect of the five fluorine atoms in aromatic ring on the heat stability of **IIc** can be explained with solvating effect of polar solvent (CH_3CN).

It was be shown earlier that activation energy increase by 36 kJ mol^{-1} on incorporating of the five fluorine atoms into aromatic ring, when thermolysis of aryl-1-hydroxy-1-hydroperoxides **Ia–Ic** (Table 1) was carried out in chlorobenzene.

Hence in studies of fluoroperoxides thermolysis the features of solvent effect on the fluorine atoms in the ring and perfluoroperoxides are observed. It is due to solvating effect described by authors [3].

The present of hydroxyl- and hydroperoxide moieties in the examined peroxides structure and thermolysis temperature range of 60–100°C are suited to the requirements made on the peroxide initiators used in condensation processes of polyester lacquers [4]. The prepared fluroperoxides can not only be used in condensation processes of polyester resins, but also for improving properties of paints and varnish covering obtained.

Table 2. Rate constants of thermolysis and activation energies of fluorine-containing aryl-1,1'-dihydroxyhydroperoxides

Compound	T, °C	$\kappa\times10^5$, s^{-1}	E, kJ mol^{-1}
IIa	40	0.71	98.3
	50	1.75	
	60	7.15	
IIb	70	2.10	86.5
	80	4.95	
	90	11.03	
IIc	70	1.83	113.91
	80	5.75	
	90	14.22	
IId	70	0.28	148.5
	75	0.58	
	80	1.19	

EXPERIMENTAL

Hydroxyhydroperoxyphenylmethane (Ia). A mixture of 10.6 g (0.1 mol) of benzaldehyde and 3.4 g (0.1 mol) of 98% hydrogen peroxide in 50 ml of anhydrous tetrachlorometane was stirred at –15 to –10°C for 1.5 h. Crystals precipitated were filtered off, washed with cold petroleum ether and recrystalled from chloroform. Yield 12.5 g (89%), mp 30–31°C. Found, %: C 60.31; H 5.99; O_{act} 11.40. $C_7H_8O_3$. Calculated, %: C 60.01; H 5.71; O_{act} 11.42.

Hydroxyhydroperoxy(4-fluorophenyl)methane (Ib) was prepared similarly from 12.4 g (0.1 mol) of 4-fluorobenzaldehyde and 3.4 g (0.1 mol) of 98% hydrogen peroxide in 10 ml of hexane. Yield 14.0 g (87%), mp 41–42°C. Found, %: C 52.93; H 4.57; O_{act} 10.21. $C_7H_7FO_3$. Calculated, %: C 53.16; H 4.43; O_{act} 10.13.

Hydroxyhydroperoxyperfluorophenylmethane (Ic) was prepared similarly from 2.0 g (0.01 mol) of perfluorobenzaldehyde and 0.3 g (0.01 mol) of 98% hydrogen peroxide in 10 ml of anhydrous pentane. Yield 1.9 g (83%), mp 105–106°C. Found, %: C 36.28; H 1.53; O_{act} 6.87. $C_7H_3F_5O_3$. Calculated, %: C 36.52; H 1.30; O_{act} 6.96.

Hydroxyhydroperoxy(2-trifluorophenyl)methane (Id) was prepared similarly from 1.7 g (0.01 mol) of 4-trifluoromethylbenzaldehyde and 0.3 g (0.01 mol) of 70–98% hydrogen peroxide. Yield 1.5 g (72%), mp 50–51°C. Found, %: C 46.32; H 3.57; O_{act} 7.61. $C_8H_7F_3O_3$. Calculated, %: C 45.71; H 3.33; O_{act} 7.62.

Di(hydroxybenzyl)peroxide (IIa). To 3.2 g (0.03 mol) of benzaldehyde was added dropwise 8.5 g (0.075 mol) of 30% hydrogen peroxide under stirring at 0–5°C. Then temperature was elevated to 20°C and held for 1 h. The precipitated product was filtered off, washed with hexane and cold ether and recrystallized from benzene. Yield 3.3 g (90%), mp 63–64°C. Found, %: C 67.96; H 5.76; O_{act} 6.49. $C_{14}H_{14}O_4$. Calculated, %: C 68.29; H 6.69; O_{act} 6.50.

Di[1-hydroxy(4-fluorophenyl)methyl]peroxide (IIb) was prepared similarly from 2.5 g (0.02 mol) of 4-fluorobnzaldehyde and 5.7 g (0.05 mol) of 30% hydrogen peroxide. Yield 2.8 g (98%), mp 77–78°C.

Found, %: C 59.26; H 4.28; O_{act} 5.76. $C_{14}H_{12}F_2O_4$. Calculated, %: C 59.57; H 4.25; O_{act} 5.67.

Di(1-hydroxyperfluorophenylmethyl)peroxide (IIc) was prepared similarly from 1.9 g (0.01 mol) of perfluorobenzaldehyde and 2.9 g (0.025 mol) of 30% hydrogen peroxide. Yield 2.1 g (96%), mp 124–125°C. Found, %: C 39.26; H 1.12; O_{act} 3.51. $C_{14}H_4F_{10}O_4$. Calculated, %: C 39.44; H 0.94; O_{act} 3.75.

Di[1-hydroxy(2-trifluoromethylphenyl)methyl] peroxide (IId) was prepared similarly from 1.7 g (0.01 mol) of 2-trifluoromethylbenzaldehyde and 2.9 g (0.025 mol) of 30% hydrogen peroxide. Yield 1.4 g (74%), mp 85–86°C. Found, %: C 39.06; H 3.91; O_{act} 5.11. $C_{16}H_{12}F_6O_4$. Calculated, %: C 39.10; H 3.85; O_{act} 5.13.

Kinetics data of thermolysis for fluorine-containing peroxide compounds **Ia–Id** were measured by iodometry method [5]. Thermolysis of peroxides **IIa–IId** was studied using the ^{1}H NMR spectroscopy on a Tesla BS-567A spectrometer (100 MHz) relative to internal HMDS.

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