A PEROXIDE THAT CONTAINS FURAN AND ACETAL FRAGMENTS

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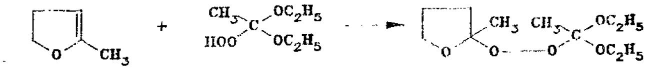
2-Methyl-2-tetrahydrofuryl(1,1-diethoxy-1-ethyl) peroxide (III) was obtained from 1,1-diethoxyethane hydroperoxide (II) and 2-methyl-4,5-dihydrofuran (I). The initiating ability of the product obtained was determined.

Peroxide compounds of the tetrahydrofuran and tetrohydropyran series, which have increased reactivities [1], are well known. It seemed of interest to study a peroxide that contains an acetal fragment, as well as a furan fragment. 2-Methyl-2-tetrahydrofuryl(1,1-diethoxy-1-ethyl) peroxide (III) was synthesized on the basis of 2-methyl-4,5-dihydrofuran (I) and the hydroperoxide of a linear acetal, viz., 1,1-diethoxyethane hydroperoxide (II), which was obtained by initiated liquid-phase oxidation with oxygen [2]:



I II III

The synthesis differed from the previously described syntheses [1] in that the reaction was carried out without an acid as a catalyst; we used a 15-50% solution of hydroperoxide II in the starting acetal. The reaction was carried out at 20-30°C with a small excess amount of the olefin, with removal *in vacuo* of the solvent and the excess olefin in the course of the reaction. The yield of peroxide III was about 95% based on the hydroperoxide.

The rate of formation of the free radicals in the thermal decomposition of hydroperoxide II and peroxide III in chlorobenzene (V_i) was determined from the rate of consumption in the free-radical-acceptor system (V_{InH}), for which we used α-naphthol (InH) [3]. Experiments with various InH concentrations demonstrated that when $[InH]_0 \geq 1 \cdot 10^{-2}$ mole/liter, V_i does not depend on $[InH]_0$ and, consequently, $V_i = 2 \cdot V_{InH}$. The initiation rate constants K_i (Table 1) do not depend on the peroxide III concentration; the temperature dependence is presented in Table 2. From the decrease in the concentration of peroxide III with time we also calculated the rate constant of its thermal decomposition (K^{Σ}), which characterizes the thermal stability of the peroxide and, in combination with K_i, the efficiency of initiation ($K_i/2K^{\Sigma}$) (Table 2).

Peroxide III can evidently be obtained by a method similar to that which we used but from 2-hydroperoxy-2-methyltetrahydrofuran and ketene acetal $CH_2{=}C(OC_2H_5)_2$ [4]. It seemed of interest to compare the thermal stability and initiating activity of peroxide III and hydroperoxides that contain one of the fragments of an unsymmetrical peroxide. According to the results presented in Table 2, the thermal stabilities of the three compounds are virtually identical, whereas the initiating ability of peroxide III is considerably greater than in the case of the starting hydroperoxides. What we observed is associated with a decrease in the contributions of chain decomposition under the influence of the radicals and the nonradical decomposition to give molecular products to the overall process on passing from hydroperoxides to peroxide III. Thus, it is more expedient to use peroxide III for the initiation of radical processes.

EXPERIMENTAL

1-Hydroperoxy-1,1-diethoxyethane (II). A 1-mole sample of 1,1-diethoxyethane was oxidized with air oxygen in the presence of 0.5 g of α,α'-azoisobutyronitrile for 20-25 h. The resulting oxidate, which contained 15% of hydroperoxide II, was washed with a 3% NaOH solution and water, dried with $MgSO_4$, and concentrated *in vacuo* at room temperature to give pure

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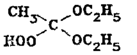
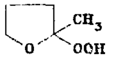
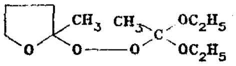
TABLE 1. Kinetic Parameters of the Decomposition of 2-Methyl-2-tetrahydrofuryl(1,1-diethoxy-1-ethyl) Peroxide (III) to Give Radicals in Chlorobenzene

T, °C	$[III]_0 \cdot 10^2$ moles/liter	$[InH]_0 \cdot 10^2$ moles/liter	$V_i \cdot 10^6$ moles/liter-sec	$k_i \cdot 10^5$ sec^{-1}
90	4,2	1,65	0,3	0,8
100	4,2	1,91	1,5	3,6
110	4,2	1,72	3,2	7,5
120	4,2	2,82	8,3	19,8
120	2,1	1,07	4,2	20,0
120	8,4	1,74	16,6	19,8
120	4,2	0,90	6,7	16,0
120	4,2	1,74	8,3	19,8
130	2,1	2,22	10,7	51,0

TABLE 2. Initiating Ability and Thermal Stability of Peroxide Compounds in Chlorobenzene

Compound	$k_i^{120°} \cdot 10^5$ sec^{-1}	E, kJ/mole	lg A	$k^{\Sigma}_{120°} \cdot 10^4$ sec^{-1}	$k_i/2k^{\Sigma}$
	5,5	104,2	9,6	1,8	0,15
 [5]	1,5	105,6	9,2	3,5	0,02
	19,8	122,3	12,6	2,5	0,40

hydroperoxide II with d_4^{20} 1.0610 and n_D^{20} 1.4194. PMR spectrum of a 20% solution of II in CCl_4 [hexamethyldisiloxane (HMDS)], δ, ppm: 1.25 m (CH_3), 4.5 m (CH_2O), and 9.2 s (OOH).

2-Methyl-2-tetrahydrofuryl(1,1-diethoxyethyl) Peroxide (III). A 2.4-g sample of 2-methyl-4,5-dihydrofuran was added to 20 g of a 15% solution of II in the acetal, after which the acetal and the excess olefin were removed *in vitro* at 30°C for 3 h to give 4.6 g of peroxide; the active oxygen content (as determined by iodometric titration) was 6.48%. The product had d_4^{20} 1.0883 and n_D^{20} 1.4608. PMR spectrum (CCl_4, HMDS), δ, ppm: 1.39 m (CH_3), 1.80 (CH_2), and 3.85 m (CH_2).

The experiments carried out with α-naphthol were conducted in a thermostated reactor with a reflux condenser in an air atmosphere. The concentrations of the inhibitor in samples selected during the reaction were determined by spectrophotometry.

In order to study the thermal decomposition, a solution of the peroxide or hydroperoxide in chlorobenzene was placed in glass ampuls, nitrogen was passed into them, and they were sealed and thermostated at the required temperature. The percentage of active oxygen in the course of the reaction was determined by iodometric titration.

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