

THERMAL DECOMPOSITION OF ESTERS OF
PEROXYDICARBOXYLIC ACIDS

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and B. A. Golovin

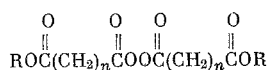
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The thermal decomposition of peroxydicarboxylic acids and their esters is a convenient method for the generation of carbonium radicals that contain the carboxyl and carbalkoxyl group [1-3]. In the present paper a study was made of the kinetics and mechanism of the thermal decomposition of the methyl esters of symmetrical aliphatic peroxy diacids, the principal products were identified, and a relation was established between the structure of the peroxides and the decomposition rate.

The peroxides were prepared from the monoesters of the semiacid chlorides of dicarboxylic acids and H_2O_2 , and their characteristics are given in Table 1; they are stable when stored, are resistant to shock and rubbing, and explode weakly in a flame. The IR spectra are in good agreement with the structure of peroxides. Three intense narrow absorption bands in the 1700-1850 cm^{-1} region characterize the vibrations of the C=O group; two bands with maxima at 1780 and 1807 cm^{-1} belong to the perturbed stretching vibrations that are characteristic for diacyl peroxides [4], while the absorption bands with a maximum at 1738-1745 cm^{-1} belongs to the stretching vibrations of the C-O group in esters. An absorption band of medium intensity in the 875-920 cm^{-1} region can be assigned to the vibrations of the O-O band.

The kinetic parameters for the thermal decomposition of peroxides in CH_3COOH and benzene are given in Table 2. The reactions obey the first order equation and the Arrhenius equation. In Fig. 1 are plotted the semilogarithmic anamorphoses of the kinetic curves for the decomposition of the dimethyl ester of peroxydiglutamic acid. Analogous linear functions were obtained for the other peroxides. As was shown in [3] using an inhibitor on the example of the dimethyl ester of peroxydisuccinic acid, induced decomposition fails to occur in these solvents. The high exponent of the preexponential factor, which has a value of the order of 10^{14} - 10^{15} sec^{-1} , testifies in support of the monomolecular mechanism.

TABLE 1. Esters of Peroxydicarboxylic Acids



Peroxide		Mp, °C	n_D^{20}	d_4^{20}	Found, %		Calculated, %		$\nu_{C=O}$, cm^{-1}	
n	R				C	H	C	H	per- oxide	ester
2	CH ₃	57	—	—	45,74	5,40	45,80	5,34	1780 1807	1740
3	CH ₃	-13	1,4514	1,1940	49,60	6,29	49,70	6,20	1780 1807	1737
4	CH ₃	-3	1,4480	1,1318	52,60	7,04	52,84	6,94	1780 1807	1738
5	CH ₃	5	1,4443	1,1020	55,66	7,63	55,49	7,50	1780 1807	1738
6	CH ₃	10	1,4440	1,0890	58,06	8,03	57,75	8,02	1780 1807	1742
8	CH ₃	24	—	—	61,37	8,98	61,75	8,75	1780 1807	1747
2	C ₂ H ₅	19	—	—	49,55	6,25	49,70	6,20	1780 1807	1731
4	C ₂ H ₅	-11	1,4436	1,0980	55,75	8,00	55,75	8,02	1780 1807	1732
8	C ₂ H ₅	22	—	—	62,90	9,22	62,88	9,17	1780 1807	1735

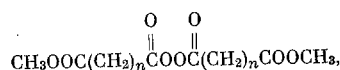
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TABLE 2. Kinetic Parameters of Decomposition of Esters of Peroxy Diacids $\text{ROC}(\text{CH}_2)_n\text{COOC}(\text{CH}_2)_n\text{COR}$ in CH_3COOH and Benzene

n	R	Acetic acid				Benzene			
		$k \cdot 10^5$ sec ⁻¹ (80°)	E, kcal/M	k_0 , sec ⁻¹	ΔS , cal /deg·M	$k \cdot 10^5$ sec ⁻¹	E, kcal/M	k_0 , sec ⁻¹	ΔS , cal /deg·M
2	CH ₃	7,1	29,2	$4,2 \cdot 10^{13}$	2,9	5,2	32,8	$3,0 \cdot 10^{15}$	12,6
3	CH ₃	16,7	31,6	$5,9 \cdot 10^{15}$	11,4	11,3	33,7	$9,0 \cdot 10^{16}$	16,7
4	CH ₃	27,2	29,4	$4,3 \cdot 10^{14}$	6,3	16,3	29,8	$4,1 \cdot 10^{14}$	6,0
5	CH ₃	30,3	29,2	$3,8 \cdot 10^{14}$	6,0	19,1	29,2	$1,3 \cdot 10^{14}$	4,9
6	CH ₃	31,4	29,0	$2,8 \cdot 10^{14}$	5,5	20,7	28,8	$1,3 \cdot 10^{14}$	3,9
8	CH ₃	32,8	29,0	$2,7 \cdot 10^{14}$	5,4	22,0	28,0	$1,9 \cdot 10^{13}$	1,7
2	C ₂ H ₅	9,3	25,9	$1,0 \cdot 10^{12}$	-5,3	—	—	—	—
4	C ₂ H ₅	30,3	30,6	$2,0 \cdot 10^{15}$	9,9	16,4	31,8	$8,2 \cdot 10^{15}$	11,0
8	C ₂ H ₅	22,2	31,4	$1,0 \cdot 10^{14}$	11,5	39,8	28,2	$5,6 \cdot 10^{15}$	3,6

In the homologous series of the esters of peroxy diacids



where $n = 2-6$ and 8 , an increase in the reaction rate constants is observed when the number of CH_2 groups increases from $n = 2$ to $n = 3$ and 4 ; k remains practically constant with further increase in $n = 5, 6$ and 8 . The lower value of k for the first members of the series is probably associated with a manifestation of the inductive effect of the carbomethoxyl groups, which is found to be in agreement with the general rule for a retardation of the decomposition of acyl peroxides under the influence of electron-acceptor substituents [5]. In Fig. 2 is plotted the half-life time ($\tau = 0.6939/k$) of peroxides as a function of the length of their carbon chain.

The activation energy (E) of the reaction for the decomposition of the esters of peroxy diacids varies in the range $28-33$ kcal/M, which in value is close to the E for the decomposition of similar unsubstituted diacyl peroxides in aliphatic hydrocarbons [6], ethylbenzene [7], benzene and CH_3COOH [8]. The highest value of E was observed for the decomposition of the esters of the peroxydisuccinic and peroxydiglutaric acids in benzene. The first two members of the series also differ in the entropy of activation.

In harmony with the existing concepts [9], the homolytic decomposition of diacyl peroxides in the solvent cage can be accomplished by three routes; with the rupture of one, two or three bonds, in which connection the character of the decomposition exerts an important effect on the composition of the formed molecular products:

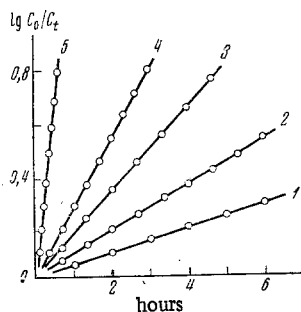


Fig. 1

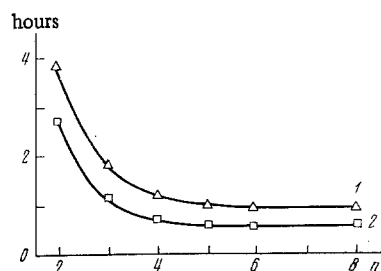


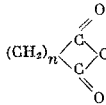
Fig. 2

Fig. 1. Semilogarithmic anamorphoses of kinetic curves for decomposition of dimethyl ester of peroxydiglutaric acid in CH_3COOH at temperature, °C: 1) 65; 2) 70; 3) 76; 4) 80; 5) 89.

Fig. 2. Half-life time of dimethyl esters of peroxy diacids $\text{CH}_3\text{OC}(\text{CH}_2)_n\text{COOC}(\text{CH}_2)_n\text{COCH}_3$ as a function of the number of methylene groups at 80° (peroxide concentration 0.075 M/liter): 1) benzene; 2) CH_3COOH .

TABLE 3. Principal Products of Thermal Decomposition of

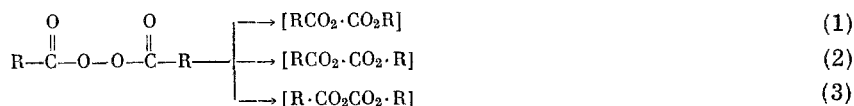
$$\text{CH}_3\text{OOC}(\text{CH}_2)_n\text{COOC}(\text{CH}_2)_n\text{COCH}_3 \text{ in } \text{CH}_3\text{COOH, M/M of Peroxide}^*$$

n	CO ₂	RCOOH†	RH	R-R	R-CH ₂ COOH	(CH ₂) _n 
2	1,52	0,30	0,10	0,57	0,20	0,18
3‡	1,50	0,21	0,31	0,33	0,18	0,28
4	1,52	0,42	0,98	0,18	0,10	—
5	1,33	0,61	0,67	0,33	0,02	—
6	0,76	1,22	0,75	Traces	Traces	—
8	0,32	1,67	0,20	"	"	—

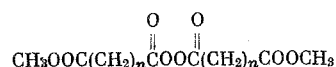
*Succinic acid was identified in all of the experiments.

†R = CH₃OC(=O)-(CH₂)_n.

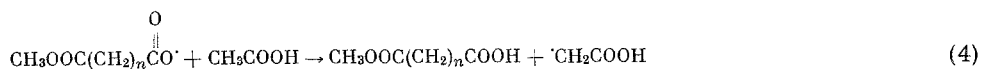
‡The yield of butyrolactone was 0.35 M/M of peroxide.



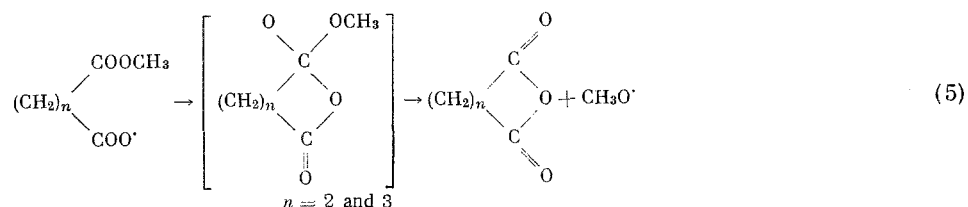
It was established that the ratio of the compounds that are obtained in the thermolysis of



in CH₃COCH is quite dependent on the value of n (Table 3). The change in the yield of CO₂ is especially sharp, and it varies from 1.52-1.50 M/M of peroxide for the first members of the series (n = 2, 3, 4) to 0.32 M/M when n = 8. The monoesters of the dicarboxylic acids are obtained in an amount that is inversely proportional with respect to the CO₂, in which connection the total yield of CO₂ and the monoester is close to the theoretical in each case, i.e., it is ~2 M/M of peroxide [taking into account the formed anhydrides of succinic and glutaric acids (see Table 3)]. As a result, under the selected conditions the decomposition of the peroxides according to reaction (1) is realized predominantly for the higher members of the homologous series, n = 6 and 8. The acetoxy radicals, which are quite stable under the experimental conditions, react with the solvent, as a result of which the half-esters of the dicarboxylic acids and carboxymethyl radicals are formed:



The anhydrides of succinic and glutaric acids were identified in the decomposition products of the methyl esters of the peroxydisuccinic and peroxydiglutaric acids, the amounts of which were respectively 0.28 and 0.18 M per mole of decomposed peroxide [10]. It is probable that they are formed as the result of the cyclization of a part of the acyloxy radicals, analogous to the situation that exists in the case of the O-(carbomethoxy) benzoyloxy radicals [11]:



Decomposition along direction (3) is more characteristic for the lower homologs in the ester series of the peroxy diacids, n = 2, 3, 4. The given conclusion is corroborated by the formation of a substantial amount of the dimethyl esters of dicarboxylic acids — the recombination products of the ω-(carboxymethyl) alkyl radicals, which is one of the important signs of cage reaction [12]. In addition, these radicals react with the solvent, being converted to the esters of monocarboxylic acids.

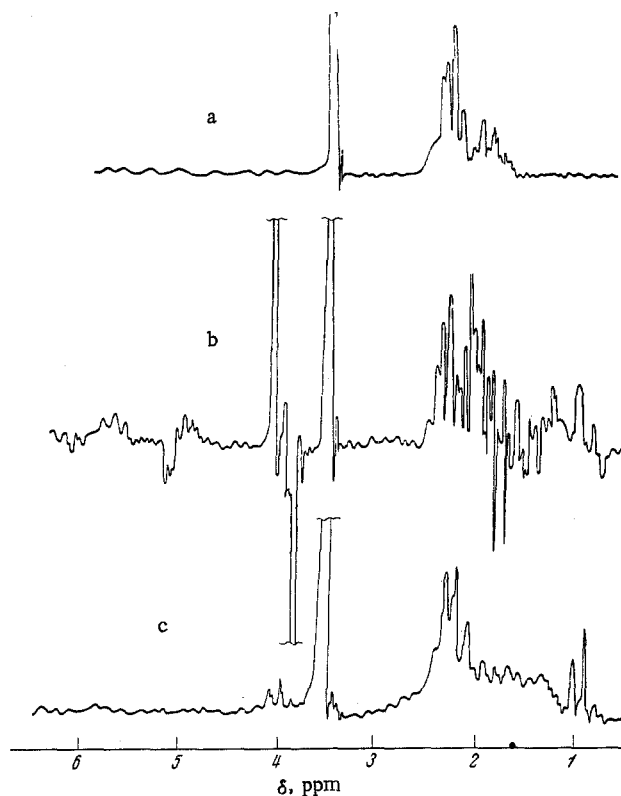
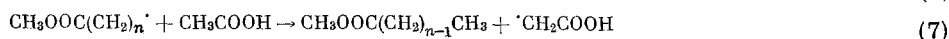
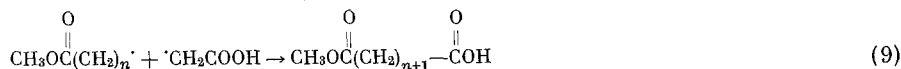


Fig. 3. NMR spectrum, obtained in the thermal decomposition of the dimethyl ester of peroxydiglutamic acid in chlorobenzene: a) starting peroxide; b) peroxide during its decomposition (after 2 min); c) spectrum of end decomposition products (after 30 min).



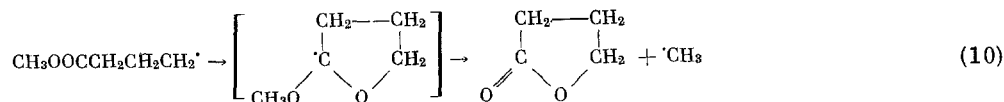
The carboxymethyl radicals, which are formed from CH_3COOH , recombine among themselves and with the alkyl radicals:



However, recombination according to Eq. (9) proceeds to a lesser degree than according to Eq. (8), despite the fact that the $\cdot\text{CH}_2\text{COOH}$ radicals are formed in substantial amount. Apparently, their amount

can be even greater than that of the $\text{CH}_3\text{-O-C}\overset{\text{O}}{\parallel}\text{-(CH}_2)_n$ radicals [as follows, for example, from the composition of the decomposition products of the peroxydipimelic and peroxydiadipic acids (see Table 3)]. This fact also testifies in support of the predominant cage mechanism of reaction (3).

While studying the decomposition of the dimethyl ester of peroxydiglutamic acid we discovered a new homolytic cyclization reaction [13]: the γ -carbomethoxypropyl radical, generated from this peroxide, is cyclized to γ -butyrolactone. The reaction possibly proceeds via the intermediate α -methoxy- α -tetrahydrofuryl radical, which undergoes β -decomposition with the elimination of the $\cdot\text{CH}_3$ radical.



The butyrolactone was identified via GLC and IR spectroscopy, and $\nu_{C=O}$ of the lactone = 1780 cm^{-1} . The radical mechanism for the formation of the lactone was established by the identification of methane in the decomposition products and by the viewing of the chemical polarization of the nuclear spins (CPN) in the NMR spectrum of the peroxide that is obtained during its decomposition (Fig. 3). The CPN effect, which relates to the protons of the β - and γ - CH_2 groups, with chemical shifts in the vicinity of 1.8 and 3.9 ppm, is found to be in agreement with the theory given in [14], which postulates transitions between the singlet and triplet (T_0) states in the radical pairs.

As follows from the quantitative composition of the formed products, the decomposition of the peroxides according to Eq. (2) probably does not take place.

EXPERIMENTAL METHOD

The IR spectra were obtained on UR-10 and UR-20 instruments. The spectra of the liquid peroxides were taken as a thin layer between NaCl plates, while the spectra of the solid peroxides were taken as Nujol mulls. The NMR spectra were obtained on a DA-60-IL instrument. The decomposition of the peroxides (10% solutions in $\text{C}_6\text{H}_5\text{Cl}$) was accomplished directly in the resonator of the spectrometer at $100\text{--}120^\circ\text{C}$.

Synthesis of Diesters of PeroxyDiacids. To a vigorously stirred mixture of 10% NaOH and 30% H_2O_2 solutions, taken in a molar ratio of 2:1, at $0\text{--}2^\circ$, was added in 30 min a double molar amount (relative to the H_2O_2) of the acid chloride of the monoester of the dicarboxylic acid. The esters of the peroxydisuccinic and peroxydisebacic acids were separated from the reaction mass by filtration, washed with 5% NaHCO_3 solution, then with chilled water, and dried in vacuo. The esters of the peroxy diacids: glutaric, adipic, pimelic and suberic, were extracted with either ether or ethyl acetate, and the extract was washed with NaHCO_3 solution, then with water, and dried over MgSO_4 . The peroxides were isolated either by freezing or by distilling off the solvent in vacuo. The dimethyl ester of peroxydiglutamic acid was also obtained by the methylation of peroxydiglutamic acid with CH_2N_2 [15], while the peroxydiglutamic acid was prepared from glutaric anhydride and 8% H_2O_2 solution [16]. The purity of the peroxides, determined from the amount of active oxygen, was 98–100% [17].

Kinetics of the Thermal Decomposition. The reactions were run in a thermostatted reactor ($\pm 0.1^\circ$) in a pure argon atmosphere, and the initial concentration of the peroxides was 0.075 M/liter. The iodometric titration of samples (5–8 measurements in one experiment) was used to determine the decomposition rate from the current concentration of the peroxides. The activation energy of the decomposition was determined from the function: $\log k$ vs. $1/T$ in the temperature range $60\text{--}80^\circ$.

Composition of Decomposition Products. The reactions were run in a 100-ml flask, and the solution concentration of the peroxide was 0.4 M/liter. The liberated carbon dioxide was collected in a trap containing caustic solution. The reaction products were analyzed by GLC on an LKhM-8M chromatograph, using detection based on the heat conductivity, a $2\text{ m} \times 4\text{ mm}$ column, either SE-30 or 10% PEGS deposited on Chromosorb W (80–100 mesh) as the liquid phase, and helium as the carrier gas. The esters of the dicarboxylic acids were analyzed directly in the decomposition products. The amounts of the monocarboxylic acids and half-esters of the dicarboxylic acids were determined after methylation of the reaction products.

The succinic and glutaric anhydrides were isolated from the reaction mixture by distilling off the low-boiling products in vacuo and subsequent recrystallization from chloroform. The structure of the anhydrides was confirmed by the elemental analysis data and the IR spectra.

CONCLUSIONS

1. We synthesized the esters of some peroxydicarboxylic acids $\text{CH}_3\text{OOC}(\text{CH}_2)_n\overset{\text{O}}{\parallel}\text{COOC}(\text{CH}_2)_n\overset{\text{O}}{\parallel}\text{COOCH}_3$, and determined the kinetic parameters of the reaction for their thermal decomposition in CH_3COOH and benzene. The predominant generation of $\text{CH}_3\text{OOC}(\text{CH}_2)_n\overset{\cdot}{\text{C}}$ radicals occurs in the decomposition of the lower

homologs ($n = 2, 3$), while the $\text{CH}_3\text{OOC}(\text{CH}_2)_n\overset{\text{O}}{\parallel}\text{C}\overset{\cdot}{\text{O}}$ radicals are obtained mainly from the higher homologs ($n = 6, 8$).

2. A new homolytic cyclization reaction was discovered, namely the formation of γ -butyrolactone from the γ -carbomethoxypropyl radicals that are obtained during the decomposition of the dimethyl ester of peroxydiglutamic acid.

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