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DECOMPOSITION OF THE PEROXIDES OF THE ESTERS OF KETO ACIDS BY Fe(II) SALTS

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 ω -Carboxy- and ω -alkoxycarbonylalkyl radicals ROOC(CH₂)_n (where R = H, CH₃ and n \geq 2) are obtained by the reduction of peroxy diacids and their esters [1, 2] or the peroxides of cycloalkanones [3, 4] by Fe(II) salts. Radicals of this type are also formed as a result of the oxidative decarboxylation of dicarboxylic acids [5, 6]. During the oxidation of ace-tic acid with Mn(III) and Ce(IV) salts carboxymethyl radicals are formed [7, 8].

In order to generate ethoxycarbonylalkyl radicals (n = 0, 1, 2) in the present work we used the reduction of peroxides, obtained from ethyl esters of keto acids and 30% hydrogen peroxide [9], with Fe(II) salts.

As is known [10, 11], the reaction of carbonyl compounds with hydrogen peroxide is accompanied by the formation of a complex mixture of products, containing α -hydroxyhydroperoxides, α, α' -dihydroxyperoxides, and gem-dihydroperoxides. The composition and yields of the products are determined by the ratio of the initial reagents and by the pH of the medium [12].

In order to establish the structure of the peroxides of the keto esters by the PMR method we obtained anhydrous samples of them by the use of ether solutions of the reagents. In the PMR spectra of the peroxides of levulinic and pyruvic acids the ratio of the integral intensities for the protons of the OH (carbon tetrachloride, δ 5.50 ppm, bs) and OOH (δ 9.70 ppm, bs) groups amounts to 1:1, and this indicates the formation of α -hydroxy- α -(ethoxycarbonyl)- and α -hydroxy- α -(β -ethoxycarbonylethyl)ethyl hydroperoxides (Ia) and (Ic). In the case of acetoacetic ester the integral intensity ratio for the OH (deuterochloroform, δ 5.65 ppm, bs) and OOH (δ 9.80 ppm, bs) groups is \sim 2:1. This fact shows that the reaction product probably consists of two substances: α -hydroxy- α -(ethoxycarbonylmethyl)ethyl hydroperoxide (Ib) and di[α -hydroxy- α -(ethoxycarbonylmethyl)ethyl] peroxide (IIb) in a ratio of \sim 2:1.

0	ОН	он он
$\operatorname{CH}_{3}C(\operatorname{CH}_{2})_{n}CO_{2}C_{2}H_{5} + H_{5}$	$_{2}O_{2} \rightleftharpoons CH_{3}C(CH_{2})_{n}CO_{2}C_{2}H_{5} +$	$C_2H_5O_2C(CH_2)_nC-OOC(CH_2)_nCO_2C_2H_5$
	оон	
n=0 (a), 1 (b), 2 (c)	(Ia c)	(IIb)

It can be supposed that the reaction of keto esters with aqueous solutions of hydrogen peroxide leads to the formation of analogous peroxy products.

The investigations into the reactions of the peroxides with Fe(II) salts were carried out in aqueous solutions obtained in the reaction of the esters of keto acids with 30% hydrogen peroxide. Stoichiometric amounts of ferrous sulfate and ferrous chloride in relation to the amount of hydrogen peroxide were used.

On the basis of data on the composition of the products (Table 1) the scheme for the decomposition of the hydroperoxides (Ia-c) can be represented by the equations:

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TABLE 1. The Products from Decomposition of the Peroxides $CH_3C(OH)(OO\dot{H})(CH_2)_nCOOC_2H_5*$ by Fe(II) Salts

		Yield of products, mole /mole of initial keto ester						
n	Salt	СН₅СООН	G2H3O2C(CH2)2 _N CO2G2H5	Ci (CH2) " CO2C2H5	CH ₃ (CH ₂) _{R-1} CO ₂ C ₂ H ₅	CH4CO4CO4C4H4 CH4COO4C4H4	CO3	other products
0	FeSO4	0,59	0,12	_		_	0,33	C₂H₅OH, 0,34;
0	FeSO₄-CuSO₄	0,59	Traces		_	-	0.58	C_2H_6 and C_4H_{10} , traces C_2H_5OH , 0.60
0	FeCl ₂	0,60	0,13	0,23		-	0,07	C ₂ H ₅ Cl, qualitative
1	FeSO ₄	0,27	0,03	-	0,11	0,07		-
1	FeSO4-CuSO4	0,27	0,02	0.10	0,13	0,10		CH.COCHCICO.C.H.
ы.	1 0012	0,21	Traces	0,10	0,11	0,00	1 -	0.06
2	FeSO ₄	0,24	0,06	1 -	0,13	- 1	_	

*Obtained by mixing equimolar amounts of ethyl esters of the keto acids and 30th hydrogen peroxide.

$$(Ia-c) \xrightarrow{Fe(II)} OH \\ (Ia-c) \xrightarrow{fe(II)} CH_3C(CH_2)_nCO_2C_2H_5 \rightarrow CH_3CO_2H + (CH_2)_nCO_2C_2H_5} \\ \downarrow O \\ (IIIa-c) (IVa-c)$$

The alkoxyl radicals (III) are also capable of being reduced by Fe(II) ions to give the initial keto ester [13]. The subsequent transformations of the radicals (IV) are determined largely by the nature of the ligand coordinated with the Fe(II) ions. During decomposition of the peroxides by the action of ferrous sulfate the generated ethoxycarbonylalkyl radicals (n = 0, 1, 2) dimerize, giving the diethyl esters of dicarboxylic acids: $2(CH_2)_n$ - $CO_2C_2H_5 \rightarrow C_2H_5O_2C(CH_2)_{2n}CO_2C_2H_5$. In addition, approximately half the radicals (IVc) take part in a hydrogen transfer reaction, as a result of which ethyl propionate is obtained. The ethoxycarbonylmethyl radicals (IVb) also abstract hydrogen from acetoacetic ester, being converted into ethyl acetate. The ethoxycarbonylacetylmethyl radicals (V) which form recombine with (IVb), giving diethyl acetylsuccinate:

 $\begin{array}{c} 0 & 0 \\ \mathbb{C}H_3CCH_2CO_2C_2H_5 + CH_2CO_2C_2H_5 \rightarrow CH_3CCHCO_2C_2H_5 + CH_3CO_2C_2H_5 \\ (IV b) & (V) \\ OCH_2CO_2C_2H_5 \\ (V) + CH_2CO_2C_2H_5 \rightarrow CH_3CCHCO_2C_2H_5 \end{array}$

In contrast to the ethoxycarbonylmethyl (IVb) and ethoxycarbonylethyl (IVc) radicals, the ethoxycarbonyl radicals (IVa) are oxidized fairly effectively by ferric sulfate to carbon dioxide and ethanol:

 $\dot{C}O_2C_2H_5 \xrightarrow{Fe(III)} [CO_2C_2H_5]^+ \xrightarrow{H_2O} CO_2 + C_2H_5OH$

A similar reaction of \cdot COOH radicals was reported in [14]. The proposed scheme is also confirmed by the formation of diethyl carbonate (identified by GLC) when the reaction is carried out in an aqueous alcohol medium (1:2):

$$[\mathrm{CO}_{2}\mathrm{C}_{2}\mathrm{H}_{5}]^{+} \xrightarrow{\mathrm{C}_{2}\mathrm{H}_{5}\mathrm{OH}} \mathcal{C}_{2}\mathrm{H}_{5}\mathrm{OCO}_{2}\mathrm{C}_{2}\mathrm{H}_{5}$$

The β -decomposition of the radicals [15] with elimination of carbon dioxide occurs to a very insignificant degree, as shown by the low yield of ethane and butane (the products from the transformation of ethyl radicals).

During decomposition of the peroxide of ethyl pyruvate in the $FeSO_4-CuSO_4$ system, the $COOC_2H_5$ radicals which form are oxidized almost completely to carbon dioxide and ethanol, and this is due to the higher oxidizing capacity of Cu(II) ions compared with Fe(III) ions. The products from oxidation of the ethoxycarbonylmethyl radicals (IVb), generated from ace-toacetic ester peroxide in the FeSO₄-CuSO₄ system, were not found.

The decomposition of the peroxides of the ethyl esters of the keto acids by the action of ferrous chloride is also accompanied by the generation of ethoxycarbonyl-substituted alkyl radicals, which are then oxidized by a ligand transfer mechanism, giving the ethyl esters of chlorine-substituted carboxylic acids:

$(\dot{C}H_2)_n CO_2C_2H_5 \xrightarrow{Fe(III)Cl} CI(CH_2)_n CO_2C_2H_5$ (IVa, b)

The radicals (IVa) are partly oxidized to carbon dioxide and ethyl chloride. In the products from decomposition of the peroxide obtained from acetoacetic ester we identified diethyl acetylsuccinate and chloroacetoacetic ester. The latter is formed by oxidation of the ethoxycarbonylacetylmethyl radicals (V) by a ligand transfer mechanism:

$\begin{array}{c} O \\ 0 \\ CH_{3}CCHCO_{2}C_{2}H_{5} \xrightarrow{F_{0}(III) Cl} CH_{3}CCHClCO_{2}C_{2}H_{5} \end{array}$

Diethyl acetylsuccinate was isolated in the pure form and identified by PMR, and the chloroacetoacetic ester was determined by GLC with a standard sample.

EXPERIMENTAL

The PMR spectra were obtained on a Varian DA-60IL instrument with TMS as internal standard. The IR spectra were obtained on a UR-20 instrument. The GLC analysis was performed on an LKhM-8MD chromatograph with a flame-ionization detector ($2 \text{ m} \times 3 \text{ mm}$ column, 12% PEGS and 15\% SE-30 on Chromosorb W, 60-80 mesh). The substances were identified against standard samples. The yields were determined by the internal standard method. The amount of carbon dioxide was determined by a gravimetric method.

Synthesis of α -Hydroxy- α -(ethoxycarbonyl)-, α -Hydroxy- α -(ethoxycarbonylmethyl)-, and α -Hydroxy- α -(β -ethoxycarbonylethyl)ethyl Hydroperoxides (Ia), (Ib), and (Ic) and Di[α -hydroxy- α -(ethoxycarbonylmethyl)ethyl] Peroxide (IIb) (General Method). A 1.6 M solution of hydrogen peroxide in ether was mixed with the stoichiometric amount of the ester of the keto acid. After 1 h the ether was distilled, and the syrupy mass was dried in a vacuum desiccator for 24 h.

PMR spectrum of the hydroperoxide (Ia) (0.2 M, carbon tetrachloride, δ , ppm): 1.34 t (3H, J = 7 Hz, CH₃CH₂), 1.46 s (3H, CH₃C \equiv), 4.30 q (2H, J = 7 Hz, CH₂CH₃), 5.50 bs (1 H, OH), 9.70 bs (1H, OOH). PMR spectrum of mixture of hydroxyperoxide (Ib) and peroxide (IIb) (\sim 0.2 M, deuterochloroform, δ , ppm): 1.23 t (3H, J = 7 Hz, CH₃CH₂), 1.45 s (3H, CH₃C \equiv), 2.75 s (2H, CH₂CO), 4.15 q (2H, J = 7 Hz, CH₂CH₃), 5.65 bs (1H, OH), 9.80 bs (1H, OOH). Ratio of integral intensities OH:OOH = 2:1. PMR spectrum of hydroperoxide (Ic) (0.2 M, deuterochloroform, δ , ppm): 1.26 t (3H, J = 7 Hz, CH₃CH₂), 1.40 s (3H, CH₃C \equiv), 2.30 m (2H, CH₂CO), 4.15 q (2H, J = 7 Hz, CH₃CH₂), 9.70 bs (1H, OOH).

Decomposition of Peroxides (Ia), (Ib) and (IIb) and (Ic). A mixture of 4.75 g (0.04 mole) of ethyl pyruvate and 4.65 g (0.04 mole) of 30% aqueous hydrogen peroxide was kept at 20°C for 2 h. A solution of 11.4 g (0.041 mole) of $FeSO_4 \cdot 7H_2O$ in 50 ml of water was then added, and after 0.5 h the solution was extracted with ether (3 × 50 ml). The content of the decomposition products was determined by GLC in the aqueous solution and in the ether extract.

The decomposition of the peroxides obtained from ethyl levulinate and acetoacetic ester by the action of FeSO₄ and FeSO₄—CuSO₄ was carried out similarly.

From the products from decomposition of (Ib) and (IIb) by the action of ferrous sulfate on a preparative chromatograph (2 m × 10 mm column, 15% PEGS on Chromaton N-AW, 40-60 mesh) we isolated diethyl acetylsuccinate. PMR spectrum (0.2 M, carbon tetrachloride, δ , ppm): 1.23 t (3H, J = 7 Hz, CH₃CH₂), 2.22 s (3H, J = 7 Hz, CH₃CO), 2.70 d (2H, J = 7 Hz, CH₂CO), 3.82 t (1 H, J = 7 Hz, CHCH₂), 4.07 q (2H, J = 7 Hz, CH₂CH₃). From the products from decomposition of (Ia) by the action of ferrous chloride by distillation we isolated ethyl chloroformate; bp 94°C. PMR spectrum (0.2 M, carbon tetrachloride, δ , ppm): 1.42 t (3H, J = 7 Hz, CH_3CH_2), 4.37 q (2H, J = 7 Hz, CH_2CH_3). IR spectrum (v, cm⁻¹): 690 (C-C1), 1150 (C-O), 1780 (CC10).

The decomposition of (Ia) by the action of ferrous sulfate in a water-alcohol solution was carried out by a similar method. A solution of 11.4 g (0.041 mole) of $FeSO_4 \cdot 7H_2O$ in 200 ml of the water-alcohol mixture ($H_2O:C_2H_5OH = 1:2$) was added to a solution of the per-oxide (0.04 mole). Diethyl carbonate was identified in the reaction mixture by GLC.

CONCLUSIONS

1. Ethyl pyruvate and levulinate react with an ether solution of hydrogen peroxide, forming α -hydroxy hydroperoxides CH₃C(OH)(OOH)-(CH₂)nCOOC₂H₅ (where n = 0, 2); acetoacetic ester gives a mixture of α -hydroxy hydroperoxide (n = 1) and α , α '-dihydroxy peroxide C₂H₅O₂-CCH₂C(OH)(CH₃)-O-OC(OH)(CH₃)CH₂CO₂C₂H₅.

2. During the decomposition of the α -hydroxy hydroperoxides by the action of ferrous sulfate and ferrous chloride the radicals $(CH_2)_n COOC_2H_5$ (n = 0, 1, 2) are generated selectively and enter into recombination, hydrogen transfer, and oxidation (when n = 0) reactions.

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