REACTION OF PEROXYDISUCCINIC ACID WITH SALTS OF METALS OF VARIABLE VALENCE

G. I. Nikishin, E. K. Starostin, and B. A. Golovin

Up to now the catalytic decomposition of diacyl peroxides was studied in organic solvents, mainly under the influence of copper salts [1-3]. In the present communication are given the results of studying the reaction of peroxydisuccinic acid (PDSA) with the sulfates of Fe^{2+} , Mn^{2+} , and Co^{2+} in aqueous solutions. In doubly distilled water, in contrast to organic solvents, the thermal decomposition of PDSA proceeds extremely slowly; approximately 160 h at 95° is required for the complete loss of active oxygen. The addition of salts leads to a sharp increase in the decomposition rate, and the reaction is ended in a matter of several minutes at room temperture.

The main decomposition products are succinic acid, propionic acid and CO_2 , and in the case of iron sulfate also adipic acid. The yield of the formed substances is indicated in Table 1. The complete decomposition of PDSA in the reaction with FeSO₄ and MnSO₄, using a stoichiometric ratio of the reactants, occurs in 5–20 min. A smaller amount of the salt slows up the decomposition of the peroxide considerably, while an excess above the stoichiometric amount has little effect on the composition and yield of the products. In contrast to FeSO₄ and MnSO₄, cobalt sulfate decomposes the peroxide completely when it is used in a catalytic amount (5 $\cdot 10^{-3}$ mole/mole of peroxide). At the end of reaction the Fe²⁺ ions are oxidized to Fe³⁺, the Mn³⁺ ions to Mn⁴⁺ (deposits as manganese dioxide), while the Co²⁺ ions do not change their valence. The liberation of oxygen is observed in the experiments with cobalt sulfate.

An analysis of the obtained data makes it possible to express some opinions regarding the mechanism of the discussed reactions. Transfer of an electron from the metal ion to the peroxide occurs in the first step, as a result of which the PDSA is decomposed into the radical and the anion:

In the solution of organic compounds, as was shown earlier [4, 5], the HOOC(CH_2)₂COO radicals decompose with the liberation of CO_2 , undergo cyclization, recombine with the carbonium radicals, and react with the solvent. In water, under the influence of $FeSO_4$, they undergo practically complete decarboxylation (approximately 1 mole of CO_2 is evolved per mole of peroxide), and the formed β -carboxyethyl radicals recombine with each other and are converted to propionic acid only to a slight degree

$$\operatorname{HOC}_{"}(\operatorname{CH}_{2})_{2} \stackrel{\circ}{\operatorname{CO}} \to \operatorname{HOCCH}_{2} \stackrel{\circ}{\operatorname{CH}}_{2} + \operatorname{CO}_{2} \tag{2}$$

In the reaction with Mn^{2+} and Co^{2+} the acyloxy radicals are probably partially reduced to the corresponding anion

$$\begin{array}{c} \operatorname{HOC} (\operatorname{CH}_{2})_{2} \operatorname{C} \dot{O} + \operatorname{M}^{n+} \to \operatorname{HOC} (\operatorname{CH}_{2})_{2} \operatorname{C} \overline{O} + \operatorname{M}^{(n+1)+} \\ \| & \| & \| \\ O & O & O \\ \end{array}$$
(5)

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Ex pt. No.	Salt	Molar ratio of peroxide: salt	Decomposition products, moles/mole of peroxide			
			CO2	acid	acid	acid
1 2 3 4 5 6 7 8 9 10*	Doubly distilled water FeSO ₄ The same ^m . MnSO ₄ The same CoSO ₄ The same "	$ \begin{array}{c} $	$\begin{array}{c} 0,43\\ 0,98\\ 0,95\\ 0,90\\ 0,12\\ 0,10\\ 0,55\\ 0,53\\ 0,46\\ 0,34 \end{array}$	$\begin{array}{c} 0,14\\ 0,10\\ 0,20\\ 0,23\\ 0,02\\ 0,07\\ 0,52\\ 0,49\\ 0,50\\ 0,32\\ \end{array}$	$1,63 \\ 0,94 \\ 0,97 \\ 0,98 \\ 1,88 \\ 1,86 \\ 1,44 \\ 1,42 \\ 1,42 \\ 1,48$	0,04 0,42 0,39 0,38

TABLE 1. Material Balance for the Decomposition of PDSA in the Presence of Salts of Metals of Variable Valence

*In Expt. 10 the gas was analyzed for oxygen, the amount of which was 0.24 mole/mole of peroxide.

The high yield of succinic acid and the slight liberation of CO_2 in the case of Mn^{2+} suggest that this step plays an important role in the overall mechanism for the decomposition of PDSA. The oxidation of Mn^{2+} to Mn^{4+} can be accomplished by two routes: the consecutive transfer of two electrons: $Mn^{2+} - e \rightarrow Mn^{3+}$; $Mn^{3+} - e \rightarrow Mn^{4+}$, and the transfer of one electron with the subsequent disproportionation of the trivalent ion: $Mn^{2+} - e \rightarrow Mn^{3+}$; $2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$. The catalytic action of Co^{2+} is explained by the high oxidation-reduction potential of the reaction: $Co^{3+} + e \rightarrow Co^{2+}$, as a result of which the reduction process with the involvement of water becomes possible [6]; $4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + 4H^+ + O_2$. In harmony with the given equation, 1 mole of oxygen is liberated when calculated on the basis of 4 moles of decomposed peroxide. The formation of oxygen was not observed when the peroxide was decomposed in the presence of Fe²⁺ or Mn^{2+} .

EXPERIMENTAL METHOD

Peroxydisuccinic acid was synthesized from succinic anhydride and 7.5% hydrogen peroxide solution [7]. Its purity, when based on the iodometric titration data, was 98-100% [8]. The decomposition of the peroxide was run in a three-necked flask, fitted with a reflux condenser and a dropping funnel. A weighed sample of PDSA (about 6 g) was placed in the flask, after which an aqueous solution of the salt was added from the dropping funnel. Argon was blown through the system prior to the start of experiment and during the course of the decomposition of the peroxide. At the end of reaction (15-20 min) the reaction mixture was heated on the water bath to effect a more complete removal of the CO_2 and O_2 . The liberated gas was collected in a gas buret and analyzed in a VTI apparatus for the amount of CO_2 and O_2 . In some of the experiments the amount of CO_2 was determined gravimetrically.

The monocarboxylic acids were isolated from the aqueous solution by steam-distillation, and were analyzed by GLC. The analysis conditions were: temperature 140-160°, length of column 2 m, the liquid phases were poly(ethylene glycol adipate) (10%) and Silicone SE-30 (8%) deposited on Chromosorb W, and the carrier gas was helium.

CONCLUSIONS

A study was made of the effect of the salts $FeSO_4$, $MnSO_4$, and $CoSO_4$ on the decomposition of peroxydisuccinic acid in aqueous medium. Both the composition and the yield of the reaction products are determined to a large degree by the nature of the metal ion.

LITERATURE CITED

- 1. S. Goldschmidt, H. Spath, and L. Beer, Ann. Chem., 649, 1 (1961).
- 2. J. K. Kochi, Tetrahedron, 18, 483 (1962).
- 3. J. K. Kochi and H. E. Mains, J. Org. Chem., 30, 1862 (1965).
- 4. G. I. Nikishin, A. T. Koritskii, and E. K. Starostin, Izv. Akad. Nauk SSSR, Ser. Khim., 386 (1970).
- 5. G. I. Nikishin, E. K. Starostin, and B. A. Golovin, Izv. Akad. Nauk SSSR, Ser. Khim., 1209 (1970).
- 6. T. Terni, Mechanisms of Oxidation-Reduction Reactions [Russian translation], Mir (1968).
- 7. V. Karnojitsky, Organic Peroxides [Russian translation], IL (1961), p. 66.
- 8. F. Critchfield, Organic Functional Group Analysis [Russian translation], Mir (1965), p. 189.