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REACTIONS OF CATALYTIC OXIDATION OF FURAN AND HYDROFURAN COMPOUNDS.

I. GENERAL PRINCIPLES OF THE OXIDATION OF FURAN IN THE SYSTEM HYDROGEN PEROXIDE – VANADIUM(IV) COMPOUNDS DEPENDING ON THE TYPE OF SOLVENT AND CATALYST

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The oxidation of furan by aqueous hydrogen peroxide catalyzed by vanadium(IV) compounds was studied in homogeneous aqueous alcohol medium and a heterogeneous system in the presence of tridecylmethylammonium chloride. The optimum conditions of the process were determined for both versions. It was shown that they are similar in direction, duration, and degree of conversion of furan. At the same time, the composition and total yield of the products, as well as their yields in the organic and aqueous phases, depend on the type of solvent and vanadium catalyst.

It is known that furan exhibits the properties both of an aromatic and of a diene system, in view of which various oxidation products can be obtained from it. Thus, in a whole series of reports devoted to the vapor phase and photochemical oxidation of furan, the possibility of its conversion to maleic acid [1] and its anhydride [2], ozonides [3], mono- and diepoxides of furan [4], β-formylacrylic acid and its esters [5, 6] has been demonstrated.

The interaction of furan with aqueous hydrogen peroxide under various conditions (at atmospheric and excess pressure, with an addition of sulfuric acid) leads to organic peroxides [1, 7] or a mixture of saturated and unsaturated mono- and dicarboxylic acids, including β-formylacrylic acid [8, 9]. It is suggested in [10] that when catalytic amounts of osmium dioxide are introduced into this system, maleic dianhydride is formed. The low yield of oxidation products is due to a large degree to the inefficiency of the indicated reactions in a heterogeneous system (furan – water) in the absence of special catalysts.

Thus, the peroxidation of furan has clearly been insufficiently studied. The new synthetic possibilities of this reaction can be realized as a result of the use of catalysts — compounds of transition metals that permit the generation of various intermediates with high oxidizing capacity from hydrogen peroxide [11]. Of special interest from this standpoint is the oxidation of furan in the presence of vanadium compounds. Earlier we established the predominant formation of 5-hydroxy-2(5H)-furanone (I) in the furfural – hydrogen peroxide – vanadium catalyst system [12]. It is suggested that compound I is the product of the main reaction pathway, which proceeds through a step of radical hydroxylation of the furan ring. The influence of a number of solvents miscible with water (acetone, ethanol, acetic acid) on the direction of this process has also been established [12, 13]. No investigations of the oxidation of furan under these conditions had previously been conducted.

Within the framework of the general strategy of searching for new synthetic possibilities of the oxidation of furan compounds, we undertook to establish the main principles of the conversion of furan in the system aqueous hydrogen peroxide – vanadium(IV) compound. In this work we present the results of a study of the influence of various organic solvents (miscible and immiscible with water) and vanadium catalysts on the course of the reaction in this system at 20°C and a molar ratio of furan – hydrogen peroxide – vanadium catalyst 1:2:0.2.

It was found that in the absence of an organic solvent the oxidation of furan under the conditions selected proceeds with low efficiency: The degree of its conversion does not exceed 15% after 20 h of reaction. Considering the low boiling point

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TABLE 1. Influence of the Nature of the Solvent and Type of Catalyst on the Oxidation of Furan in the System H_2O_2–Aqueous Alcohol–Catalyst at 20°C and Molar Ratio of Furan:H_2O_2:Catalyst Equal to 1:2:0.02

Experiment No.	Solvent	Catalyst	Time of complete conversion of H_2O_2, h	Degree of conversion of furan, %	Total yield of oxidation products,* %	
					From initial furan	From reacted furan
1	1-Propanol	$VOSO_4$	7,0	67	55	82
2	1-Butanol	$VOSO_4$	6,5	50	41	82
3†	1-Butanol	$VOSO_4$	6,5	70	49	70
4	Ethanol	$VOSO_4$	6,5	60	51	85
5	Ethanol	$VO(acac)_2$	16,0	73	52	71
6	Ethanol	$VOCl_2$	9,0	46	41	89
7	Ethanol	V_2O_4	8,0	49	33	69

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*Calculated for an arbitrary 100% yield of 5-hydroxy-2(5H)-furanone (M = 100).
†Addition of TDMAC (0.02 mole/mole of furan).

of furan, the oxidation process can be intensified mainly by increasing its concentration in the zone of formation of the active form of the oxidizing agent. We achieved this by two methods. The first of them consists of using a mixture of 30% H_2O_2 with alcohol (ethanol, 1-propanol, 1-butanol), which made it possible to conduct the reaction in a homogeneous medium of high polarity. In another version, a relatively nonpolar, water-immiscible solvent (a chlorohydrocarbon) and a catalyst of interfacial transport — tridecylmethylammonium chloride (TDMAC, 0.02 mole/mole of furan), which possesses high extractive capacity with respect to H_2O_2 [14] — were added to hydrogen peroxide of the same concentration. In all cases the initial furan concentration in the aqueous alcohol medium or chlorohydrocarbon was 8% by weight. Compounds of vanadium(IV) were used as oxidation catalysts: $VoSO_4$, $VOCl_2$, $VO(acac)_2$ and V_2O_4, which possess different solubility in water and organic solvents. The process was conducted until peroxide compounds disappeared completely in the reaction medium. The course of the reaction and the products formed were followed by chromatographic methods (gas–liquid chromatography and thin-layer chromatography).

It was found that when alcohol is added the oxidation of furan is appreciably accelerated in comparison with the addition of water (the time of complete conversion of hydrogen peroxide in this case is 6.5-7 h). Table 1 presents data reflecting the influence of the nature of the alcohol and type of the catalyst on the degree of conversion of furan, the yield of products, and the time of complete conversion of H_2O_2. Since the molecular forms of possible oxidation products of furan differ negligibly, their yield was determined calculated on the basis of an arbitrary 100% yield of compound I (M = 100) as one of the main products of the reactions that we studied.

From the data shown, it is evident that the time of complete conversion of hydrogen peroxide in the presence of $VOSO_4$ does not depend on the nature of the alcohol. At the same time, the latter factor appreciably affects the degree of conversion of furan. In 1-propanol medium, oxidation proceeds most effectively; the conversion of furan is 67%, whereas in 1-butanol medium it is only 50%. Since a mixture of hydrogen peroxide with 1-butanol was a two-phase system under the conditions selected (an aqueous solution of H_2O_2 did not mix completely with the alcohol), as we might have expected, the addition of a catalytic amount of TDMAC led to an appreciable increase in the efficiency of the process (the conversion of furan reached 70%).

The yield of oxidation products, calculated on the basis of reacted furan, proved virtually the same in experiments 1, 2, and 4. This may be evidence that their composition is approximately the same in alcohol media, which is confirmed by the data of gas–liquid chromatography and thin-layer chromatography. At the same time, in the system 1-butanol–TDMAC (experiment 3), the mass of the substances obtained was appreciably decreased, which may indicate the formation of a larger fraction of products with molecular weight less than 100 in this case.

The degree of conversion of furan, reaction time, and yield of the products in ethanol medium depend to an appreciable degree on the type of the vanadium catalyst. In the presence of $VO(acac)_2$, the conversion of the substrate is the greatest (73%); however, in this case the process is greatly slowed down. The lowest yield of the products was obtained in the experiment with V_2O_4, whereas when $VOCl_2$ was used, their yield was the greatest (89% of the reacted furan).

TABLE 2. Influence of the Nature of the Solvent and Type of Catalyst on the Oxidation of Furan in the System H_2O_2–Chlorohydrocarbon/Water–Catalyst–TDMAC at 20°C and Molar Ratio of Furan:H_2O_2:Catalyst:TDMAC Equal to 1:2:0.02:0.02

Experiment No.	Solvent	Catalyst	Time of complete conversion of H_2O_2, h	Degree of conversion of furan, %	Yield of oxidation products,* %			
					From reacted furan			Total, from initial furan
					Organic phase	Aqueous phase	Total	
8†	$CHCl_3$	$VOSO_4$	18,0	13	22	42	64	8
9	$CHCl_3$	$VOSO_4$	5,0	71	56	14	70	50
10	CH_2Cl_2	$VOSO_4$	5,0	65	23	23	46	30
11	CCl_4	$VOSO_4$	5,0	60	50	32	82	49
12	$(CH_2Cl)_2$	$VOSO_4$	5,0	50	52	24	76	38
13	$CHCl_3$	$VOCl_2$	17,0	70	47	40	87	61
14	$(CH_2Cl)_2$	$VOCl_2$	6,5	72	14	28	42	30
15	$CHCl_3$	$VO(acac)_2$	8,0	59	44	31	75	44
16	$CHCl_3$	V_2O_4	6,5	65	27	17	44	42

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*Calculated for an arbitrary 100% yield of 5-hydroxy-2(5H)-furanone (M = 100).
†Without addition of TDMAC.

Investigations analogous to those described above were also conducted on heterogeneous oxidation systems. The reaction was conducted in chlorohydrocarbon medium (chloroform, methylene chloride, carbon tetrachloride, 1,2-dichloroethane), which had previously proved to be the best solvents under conditions of interfacial oxidation [15]. From Table 2 it is evident that in the absence of TDMAC the reaction proceeds inefficiently: After 18 h the degree of conversion of furan in the chloroform–water–$VOSO_4$ system is only 13%; the bulk of the products are accumulated in the aqueous phase (experiment 8). When an interfacial catalyst is added, oxidation proceeds no less intensively than in alcohols; the general direction of the process is unchanged in this case (according to the data of gas–liquid chromatography and thin-layer chromatography).

Just as in the case of alcohols, the nature of the chlorohydrocarbon and the type of the vanadium catalyst influence the oxidation of furan in a two-phase system. Under these conditions the degree of its conversion varies within the same limits — from 50% (in 1,2-dichloroethane) to 70% (in chloroform); in the latter case the greatest yield of new products, accumulated primarily in the organic layer, is achieved (experiments 9 and 13). The reaction in CCl_4 proceeds just as efficiently, and in this case the products are accumulated chiefly in the organic layer (experiment 11).

From the data obtained, it is evident that the reactions that occur in the presence of alcohols and chlorohydrocarbons are also comparable with respect to yields of the products.

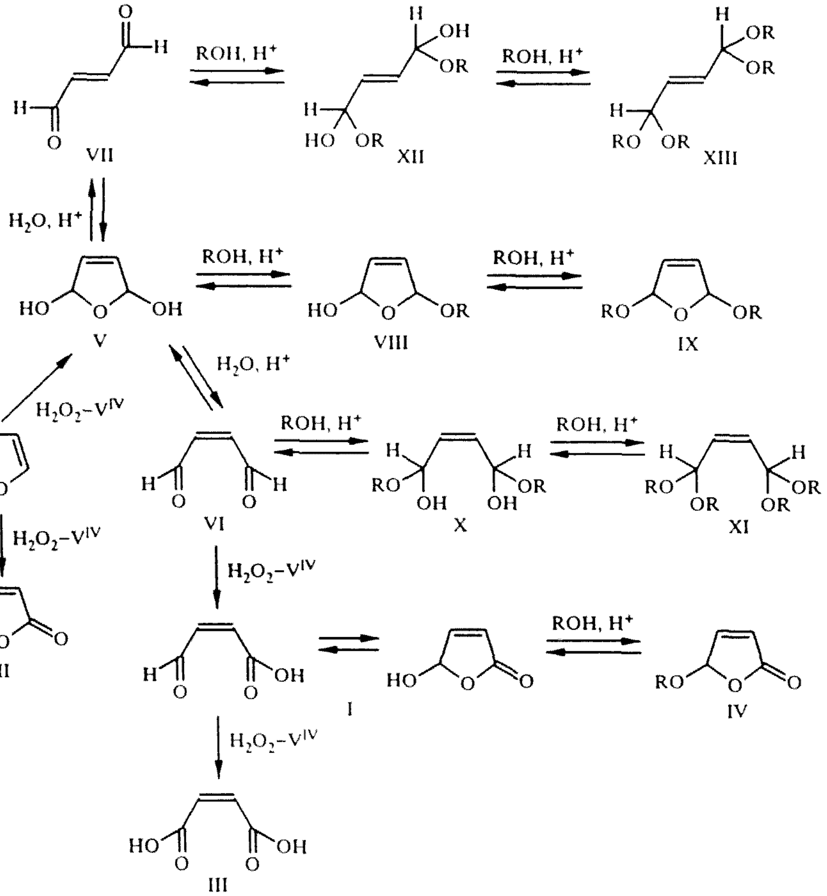
It was established that in the series of vanadium(IV) compounds studied, $VOCl_2$ is the best catalyst of the oxidation of furan in chlorohydrocarbons. Just as in ethanol medium, it permits the achievement of the greatest yield of products from the reacted substrate (87%). It is interesting that the replacement of $VOSO_4$ by $VOCl_2$ leads to an appreciable increase not only in the yield of the products but also in the reaction time, whereas in methylene chloride medium this replacement has virtually no influence on the duration of the process (experiments 13 and 14).

In a study of the composition of the reaction mixtures obtained by the methods of thin-layer chromatography and gas–liquid chromatography, using samples of hydroxyfuranone I, 2(5H)-furanone (II), and maleic acid (III) as reference standards, it was found that in all cases compound I is formed, as well as a small amount of compounds II and III, which are known to be the main oxidation products of furfural in the system H_2O_2–vanadium catalyst [12]. In aqueous alcohol media, the corresponding 5-alkoxy-2(5H)-furanones (IV), which we identified both in the reaction mixture (gas–liquid chromatography in the presence of reference standards) and in individual form (IR, PMR), are also accumulated. The products IV were isolated from the reaction mass according to the procedure developed earlier [16].

In addition to the indicated compounds, another five to eight (depending on the conditions of the reaction) other substances were also detected by chromatographic methods in the systems studied. Some of them are present both in two-phase and in aqueous alcohol mixtures and evidently are included among the main reaction products. In aqueous alcohol media, at least two to three more products are formed than in the presence of chlorohydrocarbons.

The indicated substances decolorize an acidified solution of $KMnO_4$ and form hydrazones in the reaction with 2,4-dinitrophenylhydrazine. Some of them do not react with aqueous $NaHCO_3$. This suggested that the products obtained mightinclude 2,5-dihydroxy-2,5-dihydrofuran (V) and cis-trans-C_4-dialdehydes (VI and VII), which we had previously detected as intermediate products of the reaction of furfural with H_2O_2 [17]. Using a method of determining dialdehydes VI and VII in the oxidation products of furfural (by chromatography of the 2,4-dinitrophenylhydrazones in an unfixed layer of Al_2O_3) [17], we established that they are formed in the catalytic oxidation of furan.

Considering what has been stated, as well as the fact that in aqueous alcohol systems products V – VII can form acetal and hemiacetal forms VIII – XIII, the proposed scheme of conversion of furan in the system H_2O_2 – organic solvent – water – vanadium(IV) compound takes the following form, at least according to one of the main reaction pathways:



The results obtained are evidence of the promise of the further study of the catalytic reactions of furan with hydrogen peroxide. The homogeneous (alcohol – water) and heterogeneous (chlorohydrocarbon – water – TDMAC) systems that we have proposed seem sufficiently efficient for the creation of a methodology of synthesis of new oxidation products on the basis of them.

EXPERIMENTAL

Thin-layer chromatography of the reaction mixtures obtained after the complete conversion of H_2O_2 was performed on plates of Silufol-UV 254 in the systems: chloroform; chloroform – acetone, 3:1; acetone – chloroform, 2:1; detection with acidified solutions of $KMnO_4$ and 2,4-dinitrophenylhydrazine, with an alcohol solution of bromophenol blue, and with iodine vapors.

Gas – liquid chromatography of the reaction mixture was also performed after complete conversion of H_2O_2 on a Chrom-4 instrument with flame-ionization detector and a glass column (300 × 0.3 cm). Carrier gas nitrogen, flow rate 30 ml/min. Furan and volatile products were determined on tricresyl phosphate, applied in an amount of 20% to spherochrome with particle diameter 0.2-0.3 mm; for alcohol solutions they were determined at a column temperature 70°C, evaporator 120°C, and detector 80°C; for solutions in chlorohydrocarbons the temperatures were 35, 80, and 40°C, respectively.

For an analysis of products with higher boiling points we used polymethylphenylsiloxane oil (PMPS-4), applied in an amount of 15% to Chromaton N-AW DMCS; temperature of column 150°C, evaporator 220°C, detector 220°C.

General Method of Oxidation of Furan. In a flask equipped with a mixer, thermometer, and reflux ball condenser (cooling with ice water) we placed 0.001 mole of the vanadium catalyst, 0.001 mole TDMAC (in the case of heterogeneous systems), 28.1 ml (22.5 g) of alcohol or 18.4-23.8 ml (30 g) of the chlorohydrocarbon, and 7.5 ml of a 30% aqueous solution of hydrogen peroxide. After 10-15 min, after spontaneous heating ceased, 2.5 ml (0.035 mole) of furan was added to the reaction mixture, the mixture obtained was mixed at 20°C until peroxides disappeared (development or titration with a saturated solution of KI), the mixture of products was separated from the solvent by redistillation (in the interfacial reactions, the aqueous and organic layers were separated and redistilled separately), and their weight and total yield were determined (calculated on the basis of hydroxyfuranone I).

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