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CATALYTIC OXIDATION OF FURAN AND HYDROFURAN COMPOUNDS.

6.* OXIDATION OF FURAN BY HYDROGEN PEROXIDE IN THE PRESENCE OF VANADIUM COMPOUNDS UNDER THE CONDITIONS OF PHASE-TRANSFER CATALYSIS

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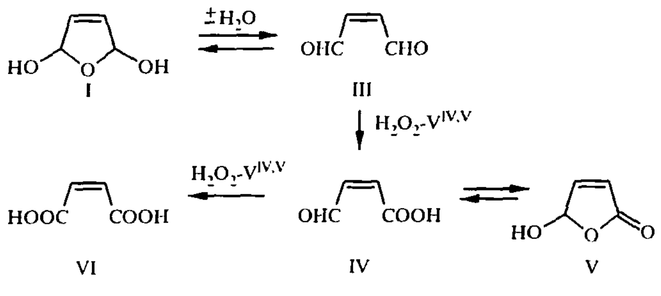
Oxidation of furan in system containing hydrogen peroxide, vanadium compound, chlorinated hydrocarbon, water, and phase-transfer catalyst was studied for the first time. In addition to the main product of this process – cis-β-formylacrylic acid – the formation of other products not previously found at oxidation of furan with hydrogen peroxide was detected. They included 2(5H)-furanone, 2,5-dihydroxy-2,5-dihydrofuran, and maleic dialdehyde. Small amounts of maleic and fumaric acids and also the product from polymerization of dihydroxydihydrofuran and dialdehyde were formed. The influence of the type of organic solvent, vanadium and phase-transfer catalysts, and the ratios of the reagents on the yield of the oxidation products were investigated.

In previously proposed mechanisms for oxidation of furan by hydrogen peroxide [2-5] it was suggested that 2,5-dihydroxy-2,4-dihydrofuran (I) is formed at the intermediate stages. However, we first detected the compound I in the products by chromato-mass spectrometry when the reaction was carried out in the presence of vanadium catalysts in aqueous ethanol [1]. It was not possible to isolate the compound I from the reaction mixture on account of its instability and small yield. At the same time diacetal of the compound I – 2,5-diethoxy-2,5-dihydrofuran (II) – was obtained under the indicated conditions with a yield of 12% [6]. In aqueous solutions dihydroxydihydrofuran I is in equilibrium with maleic dialdehyde III, which is capable of being oxidized to *cis*-β-formylacrylic acid, existing in the tautomeric forms IV and V, and then to maleic acid (VI):



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[*] For Communication 5, see [1].

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Thus, the products I, III-V are not stable in systems containing water and hydrogen peroxide. In connection with the prospect of using compounds I, III-V as synthons it seemed of interest to determine conditions of oxidation that do not promote their further transformations. In the present work we present the results of an investigation on the oxidation of furan by hydrogen peroxide in the presence of vanadium compounds in the chloroform/carbon tetrachloride–water two-phase system containing a phase-transfer catalyst.

The reaction was conducted at 20°C, the initial molar ratio of furan, 30% aqueous hydrogen peroxide, chlorohydrocarbon solvent, vanadium catalyst, and phase-transfer catalyst being 1:2:5:0.02:0.02. The type and amount of solvent and catalysts were varied in a series of experiments. The reactions and the product yields were monitored by GLC, TLC, and polarography. The process was stopped after the hydrogen peroxide had been completely consumed and the organic peroxides formed in the reaction medium had been completely transformed. The yields of compounds I, III-V were determined from the amount of 2,4-dinitrophenylhydrazones formed from them and by chromatographic methods. The total yield of the tautomers IV and V was in addition determined by polarography.

Preliminary experiments showed that the transformation of furan in the system containing hydrogen peroxide, vanadium(IV,V) compound, chlorohydrocarbon, and water is extremely ineffective in the absence of the phase-transfer catalyst (the degree of transformation of the substrate is not greater than 5%). Addition of the phase-transfer catalysts [tridecylmethylammonium chloride (TDMAC), triethylbenzylammonium chloride (TEBAC), or dibenzo-18-crown-6] to the oxidate led to an appreciable increase in the transformation degree of the substrate and to accumulation of compounds that react with 2,4-dinitrophenylhydrazine (DNPH) in the organic layer. It should be noted that the qualitative composition of the products is the same at all the types of oxidation, but the yields vary depending on the reaction conditions (Table 1). One of the main products from phase-transfer oxidation of furan is *cis*-β-formylacrylic acid (as a mixture of the tautomeric forms IV and V), the total yield of which in most experiments amounted to 35-50% of the converted substrate. The reaction products contained maleic (VI) and fumaric (VII) acids with an overall yield of up to 5% and also an appreciable amount of 2(5H)-furanone (VIII) (up to 16%). The possible formation of the latter was not foreseen in the previously proposed schemes for the oxidation of furan by aqueous hydrogen peroxide [2-5]. As seen from Table 1, *cis*-β-formylacrylic acid (forms IV and V) is distributed in almost equal proportions between the aqueous and organic phases of the final oxidates. The acids VI and VII are only present in the aqueous layer, whereas lactone VIII is in the organic layer.

In addition, the reaction mixture contained two products that accumulated mainly in the organic phase; they were revealed on Silufol plates by solution of DNPH (red-orange spots), and did not react with aqueous solution of sodium bicarbonate. The R_f values of these compounds and of the products of their interaction with DNPH (chloroform and chloroform–petroleum ether 1:1) coincided with the corresponding characteristics of the products from the oxidation of furan in water–alcohol medium and with those of malealdehyde bis(2,4-dinitrophenyl)dihydrazone (IX) [1]. The IR spectrum of solution of the detected substances in chloroform contained absorption bands at 1670 cm^{-1} and at 1705 and 1710 cm^{-1}. The first of them can be assigned to absorption of the C=C bond, whereas the other two can be assigned to absorption of the C=O groups in α,β-unsaturated aldehydes. The presence of the aldehyde groups is also confirmed by occurrence of a band at 1360 cm^{-1}. In addition, there are absorption bands in the regions of 3450 (the OH group) and 1075 cm^{-1} (the C–O–C group).

It was not possible to isolate the products on account of their instability. However, they were obtained in the form of their interaction products with DNPH, the physicochemical and spectral characteristics of which corresponded to malealdehyde dihydrazone. This, together with the TLC and IR spectral data presented above, made it possible to assign the obtained compounds to 2,5-dihydroxy-2,5-dihydrofuran (I) and malealdehyde (III). The total yield of the products I and III, determined from the amount of the hydrazone formed from them, amounted to 15-20%.

In the residue after distillation of the aqueous extract from the concentrate of the organic layer of the oxidate, containing a mixture of compounds I and III, small amount of a brownish powder poorly soluble in organic solvents and water was obtained. R_f of this product in 2:1 acetone–chloroform was 0; in its IR spectrum the bands at 3100 and 1630 cm^{-1} were observed, due to absorption of the OH and C=O groups in aldehydes with a chelate bond respectively. The presence of C–O–C bond is indicated by a set of bands in the region of 1055-1125 cm^{-1}. The band at 1670 cm^{-1} corresponding to absorption of C=C group is absent. The obtained data made it possible to suppose that the formed substance X was the product from copolymerization of compounds I and III at the C=C bonds.

TABLE 1. Results of Phase-Transfer Oxidation of Furan in the System Containing 30% Aqueous Hydrogen Peroxide, Vanadium Compound, Organic Solvent, and Phase-Transfer Catalyst (Molar Ratios of Furan, Hydrogen Peroxide, Solvent, and Catalyst 1:2:5:0.02, 20°C)

Expt. No.	Catalyst (mole/mole of furan)	Solvent	Phase-transfer catalyst	Degree of furan conversion, %	Time of complete conversion of H_2O_2, h	Yields of main products in aqueous (1) and organic (2) phases and total yield in two phases (3), %*								Overall yield of main products*
						I + III			IV + V			VI + VII	VIII	
						1	2	3	1	2	3	3	3	
1	VOSO$_4$ (0.02)	CHCl$_3$	TDMAC	60	5	2	15	17	25	21	46	2	13	78
2	VOSO$_4$ (0.02)	CCl$_4$	TDMAC	58	5	3	15	18	25	20	45	4	13	80
3	VOSO$_4$ (0.02)	CH$_2$Cl$_2$	TDMAC	56	5	—^{*2}	5	5	17	18	35	2	7	49
4	VOSO$_4$ (0.02)	1,2-DCE	TDMAC	50	5	2	13	15	23	20	43	2	14	74
5	VOSO$_4$ (0.02)	CHCl$_3$	TDMAC ^{*3}	70	4	1	19	20	28	22	50	3	16	89
6	VOSO$_4$ (0.01)	CHCl$_3$	TDMAC	35	7	2	14	16	26	22	48	1	8	73
7	VOSO$_4$ (0.04)	CHCl$_3$	TDMAC	60	4	—	—^{*2}	—^{*2}	10	22	32	5	8	46
8	VOSO$_4$ (0.04)	CHCl$_3$	TDMAC ^{*3}	85	3	—	—^{*2}	—^{*2}	20	30	50	5	16	71
9	VOSO$_4$ (0.02)	CHCl$_3$	TEBAC	36	9	—	—	—	20	5	25	5	6	36
10	VOSO$_4$ (0.02)	CHCl$_3$	CE^{*4}	30	8	—	—	—	15	5	20	2	7	29
11	VOCl$_2$ (0.02)	CHCl$_3$	TDMAC	70	10	1	14	15	34	18	52	2	15	84
12	VO(acac)$_2$ (0.02)	CHCl$_3$	TDMAC	60	8	—	10	10	31	20	51	5	10	76
13	V$_2$O$_5$ (0.01)	CHCl$_3$	TDMAC	70	5.5	—	5	5	30	20	50	4	10	69
14	V$_2$O$_4$ (0.01)	CHCl$_3$	TDMAC	75	6.5	—	—^{*2}	—^{*2}	20	7	27	5	8	40

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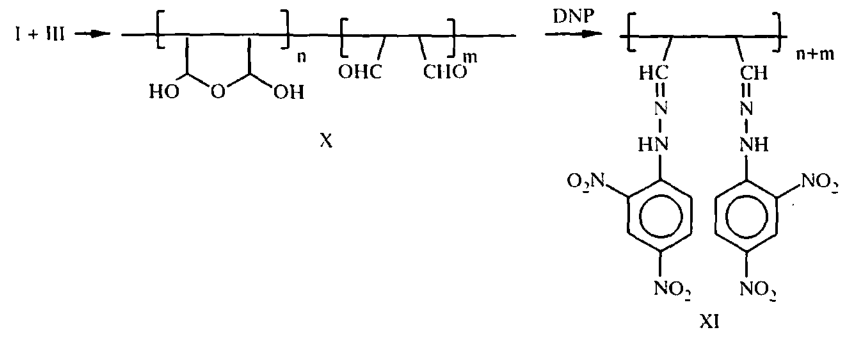
*On the reacted furan.

^{*2} The yield was lower than 0.1%.

^{*3} 0.04 mole/mole of furan.

^{*4} Dibenzo-18-crown-6.

The reaction of the polymer X with 2,4-dinitrophenylhydrazine gave yellow product XI (R_f = 0 in acetone–chloroform 2:1). Its IR spectrum, containing bands at 3310 (N–H), 1610 (C=N$_{conj}$), 1585 (C=C$_{arom}$), and 1280-1375 (Ph–NH) cm^{-1}, differs somewhat from the spectrum of dihydrazone IX (mainly in the absence of the absorption band of the C=C bond). In all probability the product XI is high-molecular hydrazone containing the elementary unit of succinaldehyde bis(2,4-dinitrophenylhydrazone).



The results presented in Table 1 indicate the possibility of controlling the yields of the products I, III-V, VIII by varying the reaction conditions. In the series of investigated organic solvents the highest yield of the products (IV+V) and (I+III) was obtained using chloroform and carbon tetrachloride (expts. 1 and 2), but their content in the organic phase was higher in the first case. For this reason chloroform, as the optimum solvent, was used in all the subsequent experiments.

Increase of the amount of TDMAC from 0.02 to 0.04 mole/mole of furan led to reduction in the reaction time, to increase of transformation degree of the substrate, and to increase in the yield of the products IV+V and I+III both total and in the organic layer (expt. 5). It is noteworthy that the ratio of the yields of the tautomers IV+V and compounds I+III was practically unchanged in comparison with expt. 1.

Reduction of the amount of VOSO$_4$ by half (expt. 6) leads to a marked decrease in the transformation degree of furan but has little effect on the yields of the main products and their proportions. At the same time if the content of the catalyst is doubled (expt. 7) the yield of these products decreased appreciably (to zero in the case of compounds I+III). However, if the amounts of vanadium and phase-transfer catalysts are increased simultaneously (in the same ratio 1:1) (expt. 8) the total yield of the tautomers IV+V and lactone is increased appreciably.

The replacement of TDMAC by the less lipophilic catalyst triethylbenzylammonium chloride (TEBAC) leads to a considerable reduction in the effectiveness of oxidation (expt. 9). Under these conditions, together with the decrease in the degree of transformation of furan and with decrease in the total yield of the products, compounds I and III are not formed at all.

In the light of data on the complexation of vanadyl acetylacetonate with dibenzo-18-crown-6 [7] we studied the possibility of transferring the vanadium peroxo complexes into organic phase by means of this crown ether. However, the latter was appreciably less effective as a phase-transfer catalyst than TDMAC – approximately at the level of TEBAC (expt. 10).

In the series of investigated vanadium(IV,V) compounds (expts. 10-14) the highest yields were obtained in the presence of VOSO$_4$ and VOCl$_2$, but in the second case the duration of the reaction was doubled. In the presence of VO(acac)$_2$, V$_2$O$_5$, and V$_2$O$_4$ the products were obtained with smaller yields. The highest effectiveness of VOSO$_4$ and VOCl$_2$ can be explained by the fact that at the beginning of the oxidation process as a result of hydrolysis they create more acidic medium in comparison with the other catalysts, which favors the accelerated formation of the highly active forms of the oxidizing agent –vanadium peroxo compounds [8].

Considering a set of such characteristics as the total yield of the products I+III and IV+V, the transformation degree of furan, and the time for complete conversion of H$_2$O$_2$ the conditions of expt. 5 (chloroform, VOSO$_4$:TDMAC = 1:2) must be recognized as being optimal in the series of investigated versions of phase-transfer oxidation of furan.

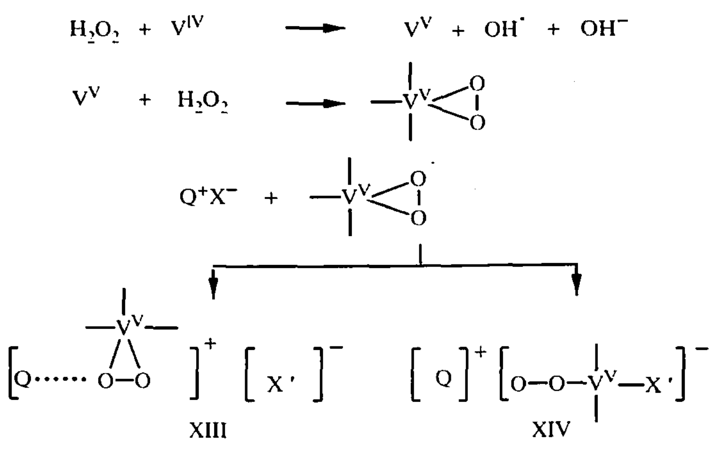
On comparison of the results from the oxidation of furan under the conditions of phase-transfer catalysis in a water–ethanol medium it is seen that the main product β-formylacrylic acid (IV+V) in both cases is formed with approximately the same yield. The main feature of the phase-transfer reaction is accumulation of a new product, i.e., dialdehyde III. In spite of the absence of ethanol, which forms the more stable diacetal II with dihydroxydihydrofuran I, the overall yield of compounds I and III in the two-phase systems does not decrease, while the yield of lactone VIII even increases. It is clear that the formation of compounds I-II and VIII under the conditions of phase-transfer catalysis is promoted by their preferential formation in the organic layer.

On the basis of the data on the composition of the products of the investigated reaction it is possible to say that the initial stages of the furan transformation in the system containing hydrogen peroxide and the vanadium compound in the presence of various solvents (ethanol and chlorohydrocarbons), the mechanism of which was discussed in detail in [1], do not differ substantially.

At examination of the factors that lead to an increase in the yield of lactone VIII under the phase-transfer conditions (compared with reaction in the water–ethanol medium) it is necessary to take account of their effect on the stage of formation and transformation of 2-hydroxyfuran (XII). Earlier we suggested that the latter is one of the key products from the oxidation of furfural and furan, which is soon transformed in two alternative directions into the stable tautomer VIII or into the products from more complete oxidation [1, 9]. Considering the proposed appreciable role of free hydroxyl radicals in the formation of the intermediate XII, the decrease in the yield of lactone VIII in the water–ethanol medium (compared with the phase-transfer reaction) can be explained by the inhibiting action of alcohol on their formation process [10]. Another factor determining the yield of lactone VIII may be its different resistance to isomeric and oxidative transformations under the various conditions. The studied reactions of furan with hydrogen peroxide differ in the type of organic solvent and in the presence of additional component (TDMAC) under the phase-transfer conditions. The effect of the solvents on the lactone VIII $\rightleftarrows$ hydroxyfuran XII equilibrium was not studied earlier in detail, but it can be supposed that the replacement of chlorohydrocarbon by ethanol promotes stabilization of the tautomer XII on account of the better solvation of its enol group by the more polar solvents (alcohol and water).

It is also necessary to take account of the possible effect of the phase-transfer catalyst on the transformations. The quaternary ammonium cation as interceptor of the $OH\cdot$ radicals is comparable in effectiveness with ethanol, and the longer its hydrocarbon chains the higher on the whole is the rate of this reaction [10]. However, in view of the overwhelming predominance of alcohol under accepted conditions in comparison with TDMAC the effect of the latter on the hydroxylation rate of furan to hydroxyfuran XII can be disregarded. A more significant factor may be the additional stabilization of compound XII as a result of its complexation (with the participation of the hydroxyl group) with the phase-transfer catalyst. As a result of this interaction the electron density on the hydrofuran XII ring must decrease, and this complicates the attack on its π-electron system by the electrophilic forms of the oxidizing agent (vanadium peroxo complexes or $OH\cdot$ radicals). Here the contribution from the concurrent isomerization of compound XII to lactone VIII must increase.

In order to explain the significant increase in the effectiveness of the furan oxidation in two-phase systems in the presence of a phase-transfer catalyst it is possible to make certain assumptions about the composition and structure of the complex intermediate responsible for the delivery of the oxidant to the organic phase. Published data [11] indicate transfer of hydrogen peroxide from the aqueous to the organic phase by means of the quaternary ammonium bases in the molecular (and not anionic) form. The production of complexes with the composition $[Q^+X^-][HOOH]$ (Q^+ is the quaternary ammonium cation, X^- is the counterion) [12] and also of adducts of quaternary ammonium salts with the peroxo compounds of molybdenum(VI) and tungsten(VI) has been reported [13, 14]. On the basis of these data and also of the results from investigation of the reactions of various organic substances with hydrogen peroxide in the presence of the transition metal (Mo, W, etc.) compounds under phase-transfer conditions [12-14] it can be supposed that complexes of the XIII and XIV types, by means of which the oxidant is delivered into the organic phase, are formed in the system containing hydrogen peroxide, vanadium compound, and TDMAC:



Q^+X^- = quaternary ammonium base; X' = Cl^-, OH^- etc.

Complex formation between vanadium (V) peroxo compound and the phase-transfer catalyst can theoretically take place both with retention of the initial structure of peroxo compound and with dissociation of the O–V^V bond. In both cases the oxidant clearly substitutes the counterion X^- in the coordination sphere of the quaternary ammonium cation; here products with various structures [of types XIII and XIV] can form. It is clear that, irrespective of the structure and empirical formula of the oxidative–catalytic complex, the nature of the anion $[X']^-$ entering it (which may in turn be the anionic part of the initial vanadium catalyst) will have a definite effect on the rate of formation of the particles XIII and XIV and their transfer into the organic phase and also on their reactivity. In the case of $VOCl_2$ and $VOSO_4$ the transfer of their peroxo forms from water to the organic layer will take place more effectively than with V_2O_5 and V_2O_4 as a result of the greater lipophilicity of the Cl^- and SO_4^{2-} anions compared with the water molecules entering into the coordination sphere of catalysts of the oxide type. In the case of $VO(acac)_2$ the bulky organic ligands of the catalyst may prevent interaction of vanadium peroxo compound with the no less bulky TDMAC molecule, and this also clearly affects the effectiveness of phase transfer.

EXPERIMENTAL

The IR spectra of the products were recorded on a Specord IR-75 spectrometer. The gas-liquid chromatograms of the reaction mixtures were obtained on a Chrom-4 instrument with a flame-ionization detector and a glass column (300 × 0.3 cm) with polymethylphenylsiloxane oil (PMPS-4), 15% on Chromaton N-AW DMCS. The carrier gas was nitrogen with a flow rate of 30 ml/min. Column temperature 150°C; injector temperature 220°C; detector temperature 220°C. The retention time of compound V was 165-172 sec. Furan was determined on the column with tricresyl phosphate, 20% on Spherochrome (particle diameter 0.2-0.3 mm). Column temperature 35°C; evaporator temperature 80°C; detector temperature 40°C.

Thin-layer chromatography of the reaction mixture and the products was conducted on Silufol UV-254 plates in chloroform and in 3:1 chloroform–acetone; the chromatograms were developed with acidified solutions of potassium permanganate and 2,4-dinitrophenylhydrazine and also with alcohol solution of bromophenol blue and iodine vapors.

The yields of the acids IV+V, VI, VII were determined by polarography using the common procedure [15]. The analyses were conducted on an LP-70 instrument in a thermostated cell with a mercury calomel electrode (m = 1.59 mg/sec, t_1 = 3.66 sec at -1.0 V) at 25 ± 0.2°C. The reference electrode was a normal calomel electrode. The supporting electrolytes were solutions of 0.1 M perchloric acid and phosphate buffer (pH 7.4).

Procedure for the Oxidation of Furan. In a flask provided with a stirrer, a thermometer, and a ball-type reflux condenser cooled with ice water under vigorous stirring we placed $(3.5\text{-}14.0)\cdot10^{-4}$ mol of the vanadium compound, $(7.0\text{-}14.0)\cdot10^{-4}$ mol of the phase-transfer catalyst, 25 ml of chloroform, and 3.75-15 ml $[(3.5\text{-}14.0)\cdot10^{-2}$ mol] of 30% aqueous hydrogen peroxide. After 5-10 min after the self-heating of the reaction mixture had ceased we added 2.5 ml ($3.5 \cdot 10^{-2}$ mol) of furan, and we stirred the mixture at 20°C until peroxides disappeared (development or titration with saturated solution of potassium iodide). To obtain solution of the products I and III in chloroform and of the polymer X the aqueous layer of the oxidate was separated and extracted 3-4 times with 5-8-ml portions of chloroform. The extracts were combined with the organic layer and dried over sodium sulfate. Chloroform was then distilled off and the concentrate was extracted with 10-15 ml of water. The aqueous extract was distilled at reduced pressure. The distillate was extracted with chloroform, and the extract was dried over sodium sulfate. A solution of the products I and III in chloroform was obtained. The residue in the distillation flask was washed with acetone and dried, and the polymer X was obtained with a yield of about 3% on the reacted furan.

The procedures for the production of hydrazones of compounds I+III and IV, V were described in [6, 16].

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