

## REACTIONS OF ALDEHYDES OF THE FURAN SERIES.

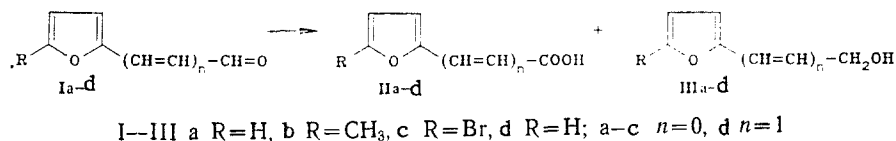
### 3.\* OXIDATIVE-REDUCTIVE CONVERSIONS ON THE SURFACE OF ALKALI GRANULES

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*Furan aldehydes undergo an oxidative-reductive disproportionation over solid alkali in a solvent inert to alkali. Molecular oxygen increases the yield of the furan carboxylic acid. A reaction scheme is proposed that takes into account the important role of alcoholates of gem-polyols.*

We established [2, 3] that furan aldehydes over solid alkali undergo a transformation with the formation of the same products as in the Cannizzaro reaction in homogeneous, aqueous solution [4; 5, p. 71]. In the present communication, we present the results of an investigation of this reaction, which takes place according to the overall scheme



The experiments were run in a round-bottom flask equipped with a fast, mechanical stirrer and a thermostat. Diethyl ether and benzene and its homologs were used as the solvent. They dissolve furan aldehydes readily and are inert toward pulverized NaOH and KOH.

In all cases, the start of the reaction was marked by a small increase in temperature (from 20 to 70°C in toluene) and a gradual buildup of suspended matter due to the stripping off of the salt forming on the surface of the granules. The process comes to a virtual halt in anhydrous solvent and at a temperature below 10°C. The introduction of 1-2 ml of water per 100 g of alkali and thermostating at 70-80°C, allows the process to finish in 1-2 h. The process was monitored by the diminution of the principal UV band of compounds Ia-d at 280, 295, 300, and 330 nm, respectively.

Two methods were used to separate the resultant heterogeneous mass of salt suspended in solvent – centrifugation and coagulation. The first method was used to investigate the composition of the salts being formed. The second was more convenient and consisted of introducing 1-2% of water into the mixture, bringing about the breakup of the suspension. The precipitate obtained was very soluble in water. On treatment of the solution with hydrochloric acid, crystals of furan carboxylic acids IIa-d precipitated. Alcohols IIIa-d were obtained from the organic solvent by distillation.

The yield of each of the products (Table 1) never exceeded 50% of the aldehyde taken, which confirms the proposed Cannizzaro disproportionation. Comparing our data with the results of carrying out this reaction in aqueous solutions [4, 5], we note a number of advantages in the preparative aspects of the method investigated. With all of the aldehydes taken, the reaction products were obtained in high yield, approaching 100% in a number of cases. In addition, it was stated in [4] that unsaturated aldehydes do not take part in a Cannizzaro reaction. The process takes place gently in heterogeneous medium without any sharp jumps in temperature. It is known [5] that in aqueous solution the yield of products IIa and IIIa does not exceed 32%, calculated for furfural, and depends strongly on the quality of the latter. Experiments we undertook with furfural containing autooxidation products showed that this had no significant effect on the yield of compounds IIa and IIIa.

\*For Communication 2, see [1].

TABLE 1. Characteristics of the Products of Disproportionation of Ia-d in Diethyl Ether over NaOH

Compound	T <sub>mp</sub> , °C	T <sub>bp</sub> , °C (mm Hg)	IR spectrum, ν, cm <sup>-1</sup>		UV spectrum (in alcohol)		Yield, %
			COOH	OH	λ <sub>max</sub> , nm	lg ε	
IIa	128		1695		244	4,05	47
IIb	108		1680		257	3,86	42
IIc	186		1680		258	4,10	48
IIId	132		1700		289	4,32	48
IIIa		68 (10)		3340	216	3,90	45
IIIb		97 (30)		3350	222	3,89	35
IIIc		90 (10)		3350	220	4,10	30
IIId		108 (10)		3360	265	4,12	47

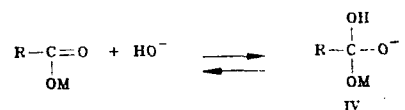
The reduced yield of products from Ib and Ic are explained by the special features of these aldehydes. Aldehyde Ib is a bifunctional compound and in an alkaline medium condensed through the methyl group to form 1,2-difuryl ethylene derivatives. This was discussed in detail earlier [6]. Alcohol IIIb is unstable and decomposed partially even during vacuum distillation, and the distilled product becomes tarry when kept for 2-3 days.

We investigated the effect of molecular oxygen on the yield of acid IIa from aldehyde Ia by passing fine oxygen bubbles through the heterogeneous mixture. Toluene was taken as the solvent, allowing the process to be carried out at 70°C. The experiments were carried out in a 2-liter flask and in a 50-liter titanium reactor. In both cases, up to 70% of acid IIa was obtained after 4 h, exceeding the calculated yield of acid from a Cannizzaro reaction.

To elucidate the nature of this phenomenon, we introduced alcohol IIIa into the reaction mixture instead of aldehyde Ia. After passing oxygen through the mixture for 2 h, we obtained 35% of IIa. By means of UV spectroscopy and GLC, the presence of up to 10% of aldehyde Ia in the mixture was established. An analogous experiment with benzyl alcohol led to the formation of a mixture containing 25% benzaldehyde and 20% benzoic acid.

These facts allow one to conclude that acid can be formed not only as the result of a disproportionation reaction, but also through the oxidation by oxygen of the aldehyde or of the alcohol being formed in the disproportionation.

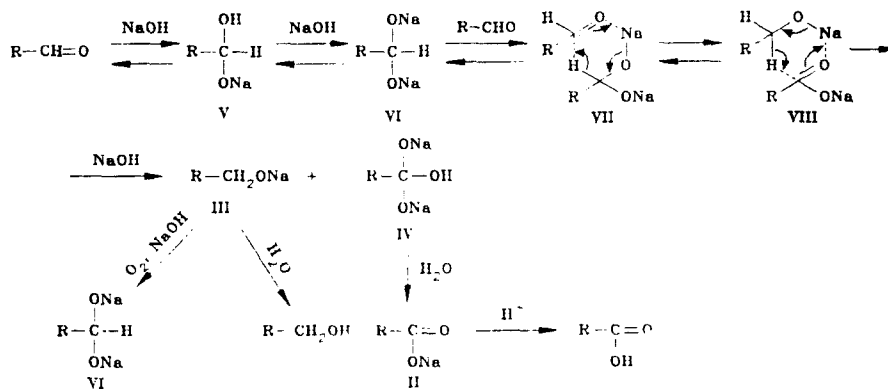
The salt forming as suspended matter in the reaction mixture from which acids IIa-d were obtained, is of interest. It has been shown by one of us [7, 8] that at high concentrations of alkali in aqueous and nonaqueous media, the salts of carboxylic acids are transformed into salts of orthocarboxylic acids, IV:



R - aryl, furyl, or other groups; M - alkali metal

It is to be expected that the salts forming in our experiments and also separating out in the precipitate when the reaction is carried out in aqueous solution [5], have an ortho structure. Elemental analysis confirmed this assumption.

According to the results obtained, the oxidative-reductive transformation of furan aldehydes on the surface of alkali granules with the formation of disproportionation products, takes place according to the scheme:



At the heat of the scheme is the idea of a hydride transfer as the chief component of the mechanism of the Cannizzaro reaction [9]. Such a transfer is possible if the reacting aldehyde molecules occur in the carbonyl and hydrate forms. It was shown [10] that, in alkaline medium, aldehydes of aromatic and heterocyclic series are partially converted into salts of gem-diols V and VI as a result of the nucleophilic addition of a hydroxyl group to the carbonyl carbon and a subsequent acid-base reaction. It is known [9] that compounds with structure VI are more prone to the oxidative loss of a hydride ion than are compounds V. The transfer reaction occurring on the surface of granules of alkali can be thought of as an isomerization of the active complex VII in which the system of intra- and intermolecular bonds facilitates the shift of electron density for the formation of less active complex VIII. The transformation of VII into VIII can be reversible. In the presence of excess alkali, complex VIII, consisting of the salts of the alcohol and the carboxylic acid, is destroyed as a result of the formation of ortho-salt IV. Passing oxygen through the mixture leads to the oxidation, in the presence of the alkali alcoholate, of monohydric alcohol III to the alcoholate of gem-diol VI and its replacement in the oxidative cycle. Product IV, which can be isolated from the reaction mixture, is converted on dissolution in water into the salt of carboxylic acid II, which is more stable in water.

In this scheme, considerable importance is attached to the role of the alcoholates of the monohydric and polyhydric alcohols, the gem-diols, as hydride ion donors. In principle, other reactions of furan aldehydes can proceed by this same mechanism. Thus, it was shown in [11] that in the oxidative-reductive reaction of furan aldehydes with alcoholates of aliphatic alcohols there is a transfer of a hydride ion complex structurally analogous to VII, as a result of which alcohols of the furan series and aliphatic aldehydes are formed.



## EXPERIMENTAL

The spectroscopic monitoring of the reaction mass was done on a Specord UV-vis spectrophotometer. The IR spectra were obtained on a Specord IR instrument.

**Synthesis of compounds IIa-d and IIIa-d** was carried out by a single method. To 0.1 mole of pulverized NaOH in 150 ml of diethyl ether are added, with vigorous stirring of the alkali, 1-3 ml of water and 0.02-0.03 mole of aldehyde Ia-d, and the ether is held at a low boil for 4 h. To the resultant heterogeneous mass 5 ml of water is added, which leads to the separation of the suspended matter into a precipitate. The ether layer containing alcohol IIIa-d is decanted, washed with water, dried with sodium sulfate, and distilled. The precipitate, consisting of ortho-salt IIIa-d, is dissolved in 50 ml of water and the solution is acidified with 5 ml of concentrated HCl. The precipitated product is recrystallized from heptane and dried in air.

When benzene and its homologs are used as solvent, the synthesis is carried out in analogous fashion. A fractionating column is used in distilling the oil containing the furfuryl alcohols.

**Pyromucic Acid (IIa).** A. A stream of fine bubbles of molecular oxygen is passed at a rate of 6-10 liters/h through a vigorously stirred mixture of 1 mole of NaOH or KOH in 500 ml of toluene at 60-70°C. To this reaction system, equipped with a reflux condenser, is added 0.4 moles of furfural over a 30-min period. The mixture is then thermostated for 3 h while oxygen continues to be passed through it. The solid is separated out, dissolved in water, and acidified with HCl to give 30 g (0.27 mole) of IIa (67% of the Ia taken).

B. Into the same mixture of reactants 0.4 mole of furfuryl alcohol is poured instead of furfural. The reaction proceeded in analogous fashion to give 16 g (0.14 mole) of IIa (35% of the IIIa taken). UV spectroscopy and GLC in toluene established the presence of 4 g of Ia (0.04 mole).

**Disodium Orthofuroate (IVa).** The reaction mixture obtained in the synthesis of IIa by one of the methods described above is centrifuged. The solid material settled out is further washed with ether and dried in a vacuum desiccator. The cream colored product does not melt below 600°C, is very soluble in water, and stable when kept in air. Found, %: C 33.0, H 2.2, Na 24.6.  $C_5H_4O_4Na_2$ . Calculated, %: C 33.4, H 2.8, Na 26.4.

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## REDUCTION OF ALDEHYDES OF THE FURAN SERIES BY THE METHOD OF CATALYTIC HYDROGEN TRANSFER

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*The intermolecular transfer of hydrogen from donor molecules to aldehydes of the furan series is studied in the presence of homogeneous, complex  $[Ru(PPh_3)_3Cl_2]$  and heterogeneous (Pd/C) catalysts. A linear correlation is obtained between the reactivity of the furan aldehydes and the nature of the substituent.*

Catalytic, intermolecular hydrogen-transfer reactions have been very often used recently along with the familiar method of catalytic hydrogenation with molecular hydrogen in order to reduce organic compounds.

The basic results of reducing unsaturated bonds and functional groups by the use of different hydrogen donors, solvents, and catalysts have been generalized in several reviews [1-3].

Alcohols are most widely used as hydrogen donors. With their help, for example, in the presence of Raney nickel [4] and zirconium oxychloride [5], the carbonyl group of aldehydes and ketones is reduced. In [6], the reduction of aldehydes and ketones with 2-propanol in the liquid phase using zirconium oxide was described. At the boiling point of 2-propanol, which is simultaneously the solvent and hydrogen donor, furfural, together with other aldehydes and ketones, is reduced to furfuryl alcohol, which is formed in 99% yield when the reaction is prolonged for 6 h. Hydrogen transfer took place on the reduction of dimethyldi(2-furyl)germane in the presence of Raney Ni at 120°C. When a Pd/C catalyst was used, transfer was effected only from cyclohexene [7]. The reduction of aldehydes and ketones by alcohols is also effectively catalyzed by the metal complexes  $Co(PPh_3)_3H_3$  [8],  $Ru(PPh_3)_3Cl_2$  [9-12],  $Rh(PPh_3)_3Cl$  [12, 13], and  $Ru(PPh_3)_3H_2$  [14, 15].

In the presence of heterogeneous, palladium catalysts for the reduction of aromatic carbonyl compounds, cyclohexene, along with alcohols, can serve as a hydrogen donor [16-18].

One of the extremely effective hydrogen donors for the reduction of the carbonyl group is formic acid, at the carbon atom of which there is a hydrogen that possesses marked hydridic mobility. The reduction of carbonyl compounds with the aid of formic acid in the presence of ruthenium complexes as catalysts, is described in [19]. Aliphatic, alicyclic, and aromatic ketones and aldehydes under hydrogen transfer conditions are also reduced in the presence of excess formic acid, a tertiary amine, and compounds of Group IVA metals –  $Cp_2ZrCl_2$ ,  $Cp_2TiCl_2$ ,  $Cp_2HfCl_2$ ,  $CpZrCl_3$ ,  $ZrCl_4$ , and  $Cp_2ZrH$  – as catalysts [20]. According to [21], the system  $HCOOH-(C_2H_5)_3N-Ru(PPh_3)_3Cl_2$  selectively reduced aldehydes to the corresponding al-

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