STUDY ON THE CATALYTIC OXIDATION WITH AIR OF FURANE DERIVATIVES SUBSTITUTED IN THE α POSITION

By

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In our earlier communications [1—3] we reported that we succeeded to prepare catalysts with favourable properties for the catalytic oxidation with air of carbohydrates, and that these catalysts were suited for the oxidation of di-O-*iso*-propylidene hexoses and 0-*iso*-propylidene hexoses, yielding the corresponding monocarbonic acid. In the oxidation of the latter compounds, however, by-products are also formed under certain conditions. Among these, the formation of oxalic acid can readily be followed.

Since all investigated sugar derivatives were compounds containing the furanose or pyranose ring, a further simplification of these models could be achieved by studying the catalytic oxidation with air of furane derivatives.

In the present paper we shall discuss catalytic oxidation with air of the model compounds tetrahydrofurfuryl alcohol (THFA), furfuryl alcohol (FA), furfural (F) and α-methylfurane (MF). The aim of oxidation was in all cases to prepare the corresponding furane-α-carbonic acid. The experimental procedure was the same as developed in our previous work on di-O-*iso*-propylidene hexoses.

Oxidation in acid solution does not lead to the formation of furane-α-carbonic acids [4].

Brown [5] oxidized furfural, furfuryl alcohol and 2-methylfurane with potassium iron(III)cyanide in a solution containing KOH. The furane-α-carbonic acid yields were 22%, 21% and 5%, resp.

Hideo Arita and co-workers [6] obtained furane-α-carbonic acid with a yield of 98% by oxidizing furfural with sodium hypochlorite. This path is also applicable for the oxidation of sugars.

Salkhinkin and Lapkova [7] carried out oxidation with sodium hypobromite and achieved a yield of 64%.

Ko and Hideo [8] oxidized furfural with hydrogen peroxide to furane-α-carbonic acid with a yield of 96%.

Oxidations using solid catalysts in aqueous alkaline solution and a chemical oxidant or oxygen are also known.

Kiyoko Takahai [9] oxidized furfural to furane-α-carbonic acid with chlorates in the presence of Mn_2O_3, Al_2O_3 or Fe_2O_3 catalyst.

Dunlop [10] introduced oxygen into an aqueous alkaline solution of furfural at 50 to 60 °C. The catalyst contained Ca, Ni, Fe, Ag, Pt and Au (mainly oxides).

Cadiglona and Piacenza [11] used an MnO_2 catalyst activated with Ag_2O for this purpose.

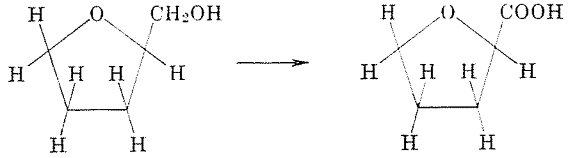
Adrisano [12] oxidized a 5% by weight aqueous alkaline solution of furfural to furane-α-carbonic acid with a yield of 91%, using oxygen and an Ag_2O catalyst.

Other authors, namely Dinelli [13], Okada and co-workers [14] and Montegna and McQuillon [15] found that copper oxide containing traces of silver was also suitable as catalyst.

Ryuichi and co-workers [16] observed that yield depended on the conditions of catalyst preparation. Optimum temperature was 30 °C and yield was directly proportional to the quantity of catalyst.

Okado and Kutamura [17], using a mixture of Ag_2O and CuO on pumice support, stated the rate of reaction to be proportional to the concentration of furfural, but was not affected by the mass flow between gas — liquid and liquid — solid phases.

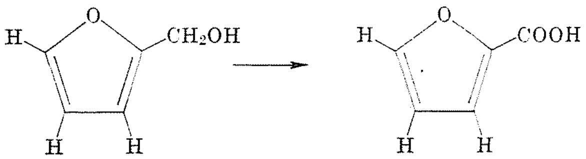
The first compound whose oxidation we investigated was tetrahydrofurfuryl alcohol, yielding, as expected, tetrahydrofurane-α-carbonic acid:



Yield was good (92%), no by-products formed.

Oxidations were carried out at different temperatures (Fig. 1), indicating that the rate of reaction was maximum at 50 to 60 °C (Fig. 2). The Arrhenius plot (Fig. 3) gave an apparent activation energy of 3.2 kcal/mol (between 45 and 55 °C). Oxidations in solutions with different initial concentrations (Fig. 4) indicated that the rate of oxidation *vs.* concentration passed through a mild maximum (Fig. 5). These findings indicate great similarity to the oxidation of MAG and D-glucose.

The next simple model compound differing from THFA only in the aromatic character of the ring was furfuryl alcohol, yielding furane-α-carbonic acid with a yield of 83%:



Oxidation was studied at various temperatures (Figs 6 and 7). The rate of oxidation is maximum at 40 to 50 °C (Fig. 8). Apparent activation energy calculated from the Arrhenius plot (Fig. 9) is 3.7 kcal/mol.

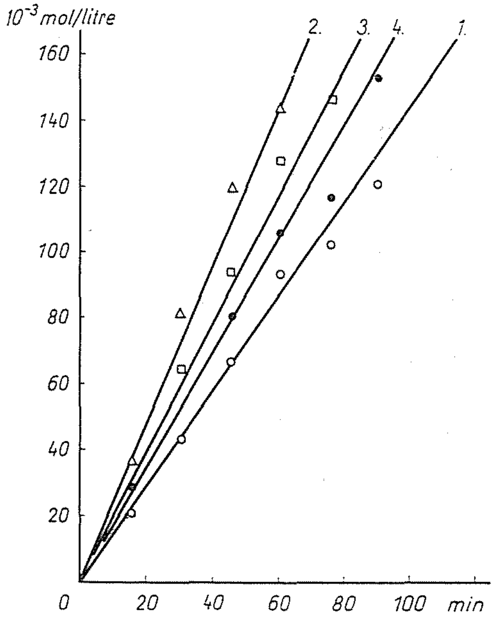


Fig. 1. Oxidation of tetrahydrofurfuryl alcohol *vs.* time at different temperatures. 1 — 40 °C 2 — 56 °C; 3 — 66 °C; 4 — 76 °C

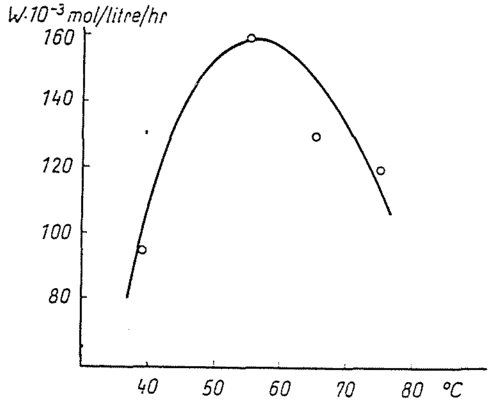


Fig. 2. Rate of tetrahydrofurfuryl alcohol oxidation *vs.* temperature

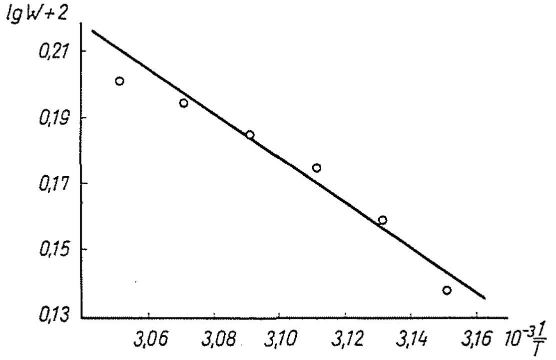


Fig. 3. Logarithm of the rate of tetrahydrofurfuryl alcohol oxidation *vs.* 1/T (45—55 °C)

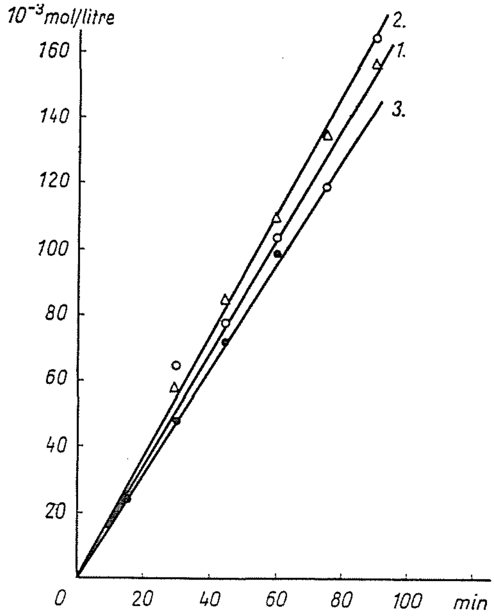


Fig. 4. Oxidation of tetrahydrofurfuryl alcohol *vs.* time at different initial concentrations. 1 — 190.0 · 10^{-3} mol/litre; 2 — 264.0 · 10^{-3} mol/litre; 3 — 362.0 · 10^{-3} mol/litre

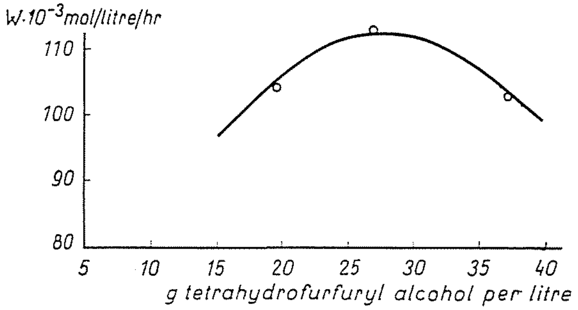


Fig. 5. Rate of tetrahydrofurfuryl alcohol oxidation *vs.* concentration

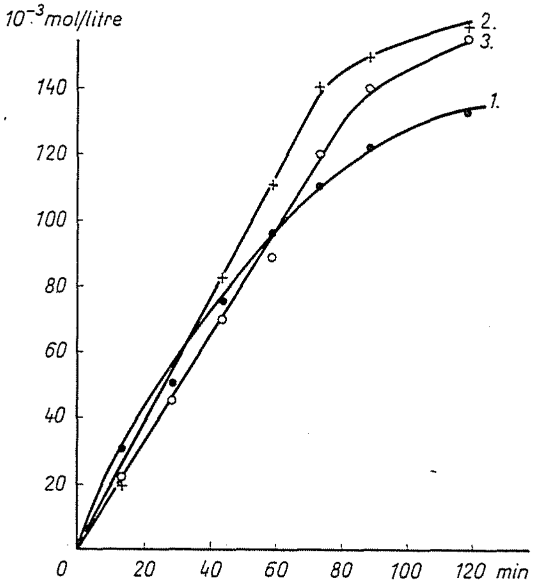


Fig. 6. Oxidation of furfuryl alcohol *vs.* time at different temperatures. 1 — 33 °C; 2 — 42 °C; 3 — 52 °C

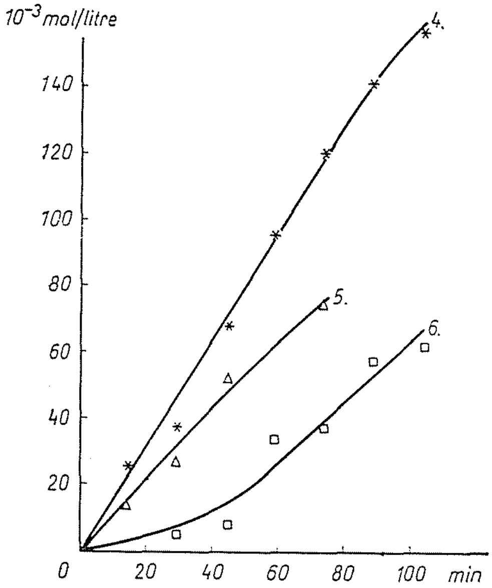


Fig. 7. Oxidation of furfuryl alcohol *vs.* time at different temperatures. 4 — 52 °C; 5 — 76 °C; 6 — 93 °C

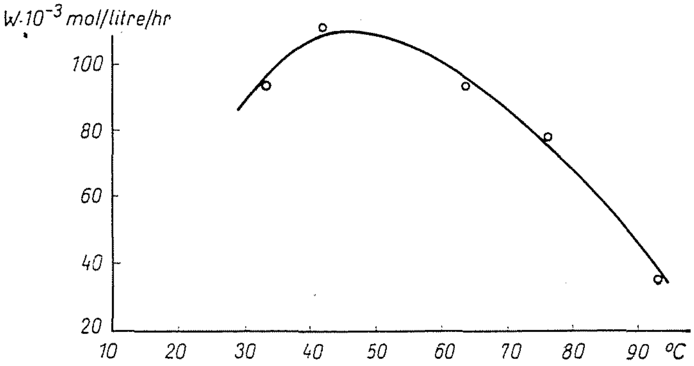


Fig. 8. Rate of furfuryl alcohol oxidation *vs.* temperature

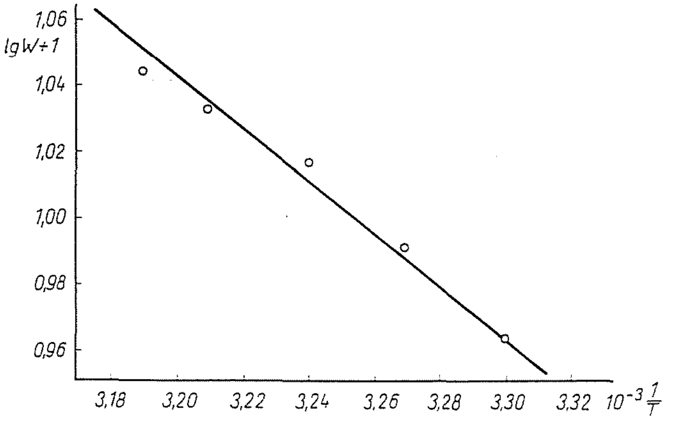
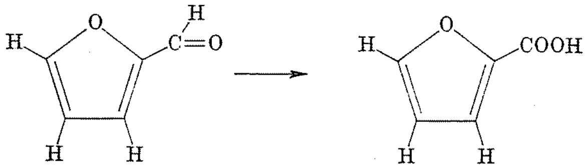


Fig. 9. Logarithm of the rate of furfuryl alcohol oxidation *vs.* 1/T (30—42 °C)

Rate of reaction *vs.* concentration yields a curve with a maximum in this case too (Figs 10 and 11).

The results are similar to those obtained with THFA. Chemical differences appeared not to affect the rate of oxidation. However, to decide this question, the oxidation of other substrates was also investigated.

Studies on the oxidation of THFA and FA necessarily led to the study of the oxidation of furfural, a compound of remarkable interest also from the industrial view. The oxidizable group of furfural is the carbonyl group:



The reaction product, viz. furane-α-carbonic acid was obtained with yields exceeding 90%. No by-products were formed in the oxidation.

We studied the oxidation of furfural at various temperatures (Figs 12 and 13). The rate of reaction has a maximum at 40 to 50 °C (Fig. 14). Apparent activation energy calculated from the Arrhenius plot between 28 and 40 °C (Fig. 15) is 3.3 kcal/mol.

Oxidation was also studied in solutions with different concentrations (Fig. 16). Concentration dependence of the rate of reaction, similarly to the previous cases, gave a maximum curve (Fig. 17).

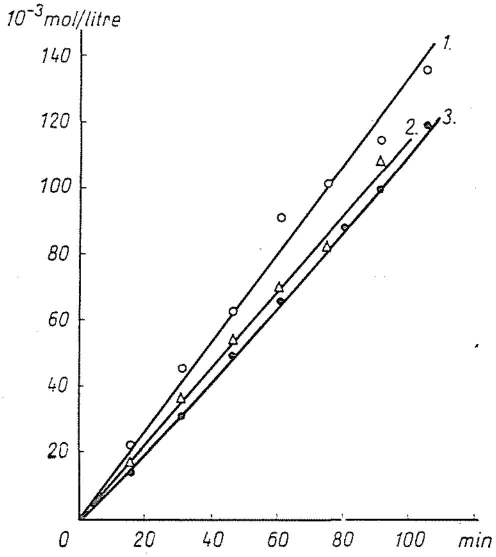


Fig. 10. Oxidation of furfuryl alcohol *vs.* time at different initial concentrations 1 — 191.0 · · 10^{-3} mol/litre; 2 — 261.0 · 10^{-3} mol/litre; 3 — 349.0 · 10^{-3} mol/litre

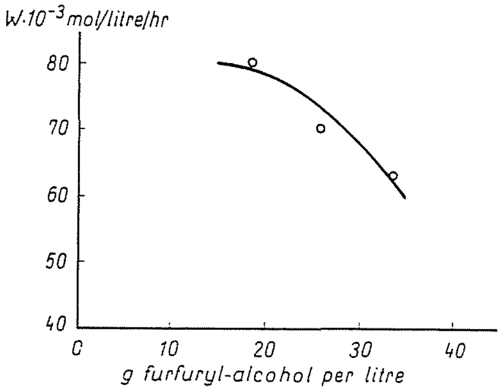


Fig. 11. Rate of furfuryl alcohol oxidation *vs.* concentration

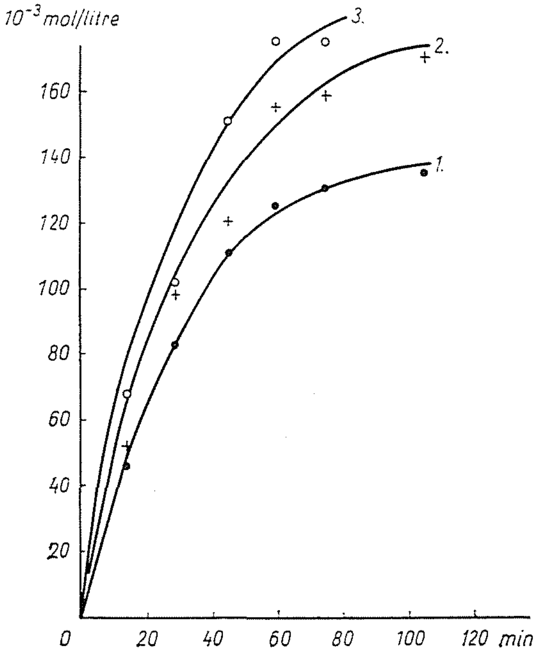


Fig. 12. Oxidation of furfural *vs.* time at different temperatures 1 — 20 °C; 2 — 30 °C; 3 — 40 °C

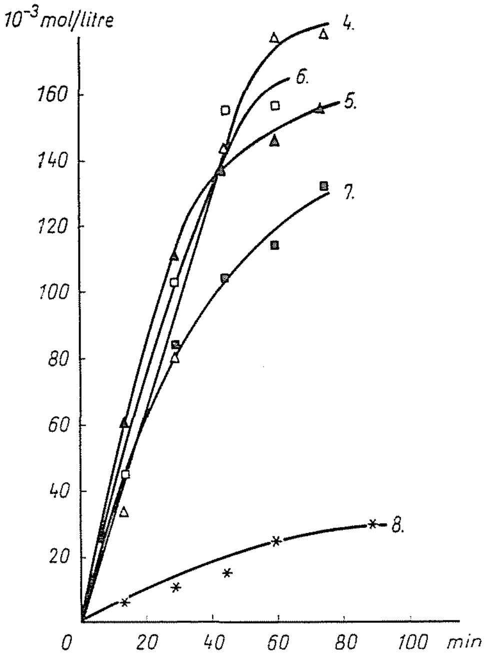
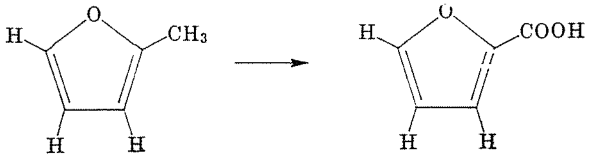


Fig. 13. Oxidation of furfural *vs.* time at different temperatures 4 — 50 °C; 5 — 60 °C; 5 — 60 °C; 6 — 70 °C; 7 — 80 °C; 8 — 90 °C

The following model compound investigated was α-methylfurane. This was of interest, because it allowed to decide whether our process suited the oxidation of the methyl group to the carboxyl group:



The oxidation of MF yielded furane-α-carbonic acid without any by-product. Yield was close to 60%. The lower yield can be explained by the poor water solubility of MF under the conditions of oxidation, so that the reaction mixture will consist of four phases.

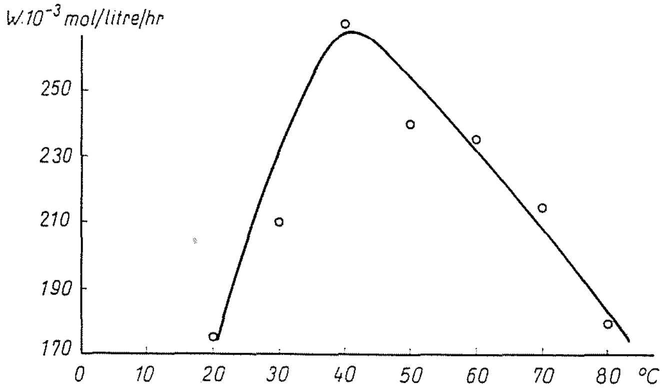


Fig. 14. Rate of furfural oxidation *vs.* temperature

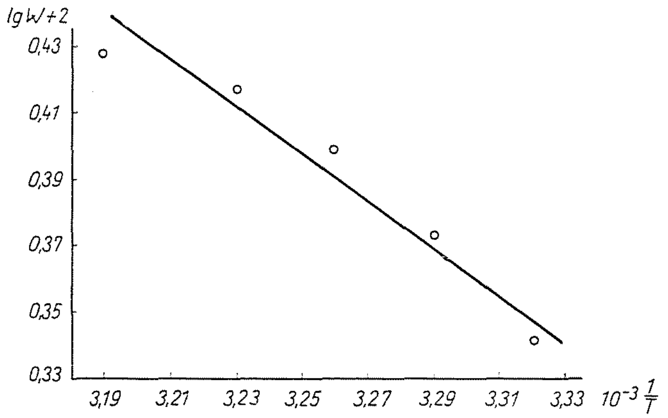


Fig. 15. Logarithm of the rate of furfural oxidation *vs.* 1/T (28—40 °C)

Oxidation experiments at various temperatures (Fig. 18) showed the rate of oxidation to have a maximum around 40 °C in this case too (Fig. 19). The Arrhenius plot (Fig. 20) yields a value of 10.0 kcal/mol for apparent activation energy. This value significantly differs from the values found for other furane derivatives.

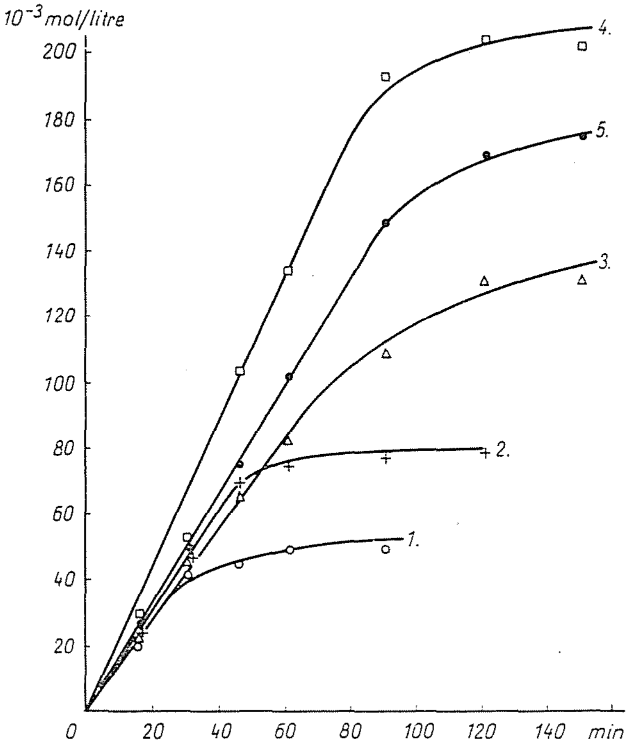


Fig. 16. Oxidation of furfural *vs.* time at different initial concentrations. 1 — 52.0 · 10^{-3} mol/litre; 2 — 104.0 · 10^{-3} mol/litre; 3 — 191.0 · 10^{-3} mol/litre; 4 — 261.0 · 10^{-3} mol/litre; 5 — 364.0 · 10^{-3} mol/litre

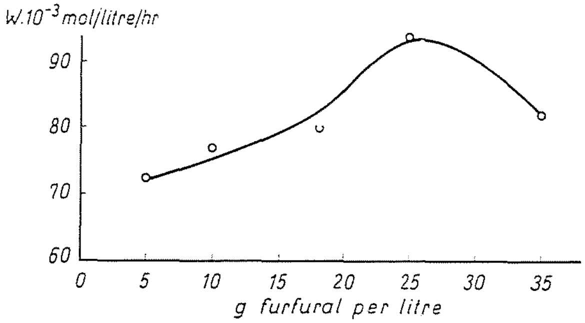


Fig. 17. Rate of furfural oxidation *vs.* concentration

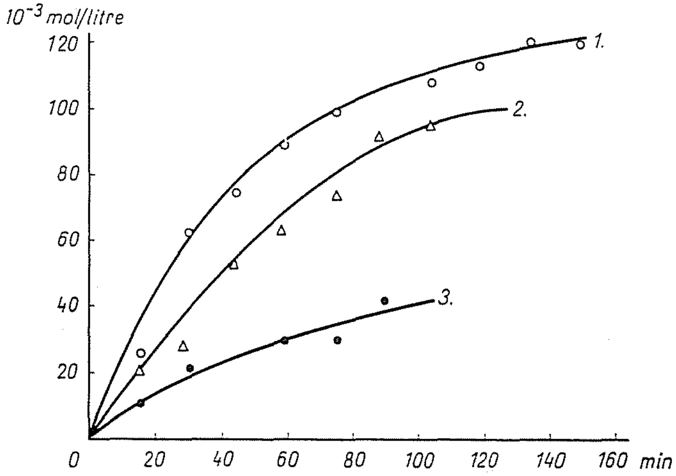


Fig. 18. Oxidation of 2-methylfurane *vs.* time at different temperatures. 1 — 40 °C; 2 — 43 °C; 3 — 47 °C

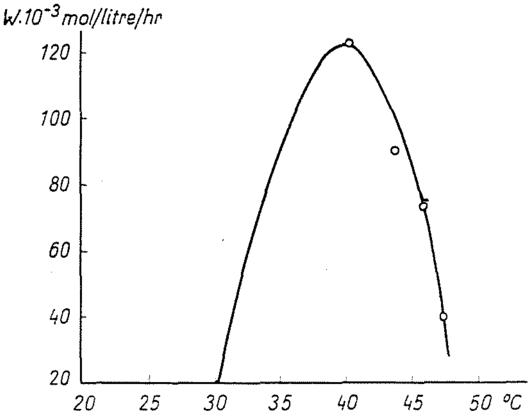


Fig. 19. Rate of 2-methylfurane oxidation *vs.* temperature

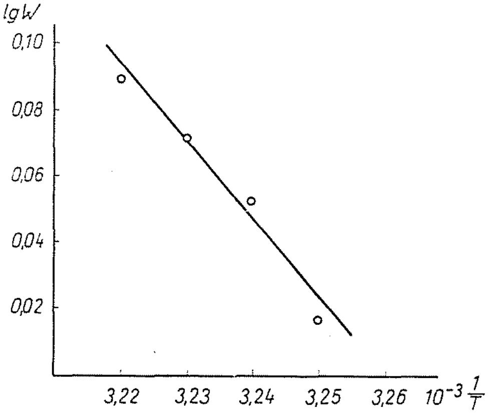


Fig. 20. Logarithm of the rate of oxidation of 2-methylfurane *vs.* 1/T (35—38 °C)

Also, the relationship between rate of reaction and concentration (Figs 21 and 22) differs from the results obtained with the other furane derivatives: in the case of α-methylfurane, the rate of reaction decreases with increasing concentration.

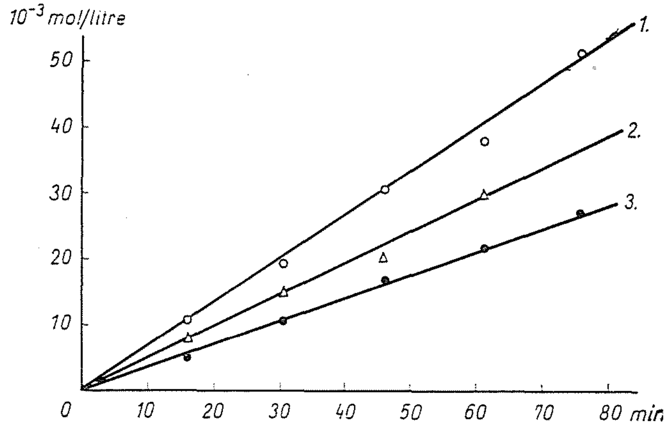


Fig. 21. Oxidation of 2-methylfurane *vs.* time at different initial concentrations. 1 — 131.0 · 10^{-3} mol/litre; 2 — 192.0 · 10^{-3} mol/litre; 3 — 267.0 · 10^{-3} mol/litre

Summing up, the results allow to state that furane derivatives substituted in the α position are readily oxidized with our catalysts and procedure. No difference was found between the oxidation of the —CH_2OH group, whether attached to tetrahydrofurane or to furane. The situation was similar when the —CHO group was attached to furane. A difference was found only in the case of the —CH_3 group, this, however, being explainable by the four-phase reaction mixture with α-methylfurane.

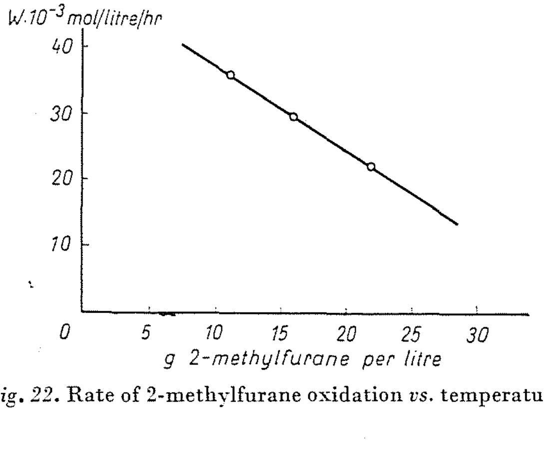


Fig. 22. Rate of 2-methylfurane oxidation *vs.* temperature

Maxima of the rate of oxidation are found around 60 °C and at concentrations of about 200 mmol/litre. The values of apparent activation energy are between 3.2 and 3.7 kcal/mol. All these values are much similar to the values found with O-*iso*-propylidene hexoses and hexoses.

Summary

The palladium catalysts on bone black support developed by us and well suited for catalytic oxidation with air, in aqueous alkaline solution, of di-O-*iso*-propylidene hexoses, O-*iso*-propylidene hexoses and hexoses, have now been tested for their suitability in the catalytic oxidation with air of tetrahydrofurfuryl alcohol, furfuryl alcohol, furfural and α-methylfurane. The corresponding monocarbonic acids were found to form in the reaction. Yields were around 90%, in the case of α-methylfurane only 60%. The rate of oxidation plotted against temperature and concentration yields curves passing through a maximum.

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