STUDY ON THE CATALYTIC OXIDATION WITH AIR OF 1,2-O-iso-PROPYLIDENE-α-D-GLUCOFURANOSE AND D-GLUCOSE

By

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Our previous communications reported of the study of the preparation of catalysts [1] in whose presence di-0-*iso*-propylidene hexoses having a free primary hydroxyl group are readily oxidized with air, in aqueous medium, to the corresponding monocarbonic acids [2].

The present paper will discuss the utilization of these catalysts, making use of our earlier experiences, for the oxidation of an O-*iso*-propylidene hexose having, in addition to the free primary hydroxyl group, a free secondary hydroxyl group. As model compound 1,2-O-*iso*-propylidene-α-D-glucofuranose (MAG) has been chosen. We also studied the action of the catalysts in the oxidation of a hexose in which all hydroxyl groups are free. As model compound, for better comparison's sake, we chose D-glucose (G).

In experimental work we followed the method developed in previous studies for di-O-*iso*-propylidene hexoses.

Trenner [3, 4] oxidized MAG with air, in the presence of platinum catalyst on bone black, in aqueous solution containing sodium hydrogen carbonate, to the corresponding monocarbonic acid.

Mehltretter and co-workers [5] carried out this oxidation with a 13% by weight catalyst on bone black, at 50 °C, in the course of 7 to 11 hours. After hydrolysis the yield of D-glucuronic acid was 38%. Colon and co-workers [6] achieved a yield of 50% at 70 °C.

Tulchinsky [7] oxidized D-glucose to D-gluconic acid with potassium bichromate in sodium carbonate solution between 80 and 90 °C.

Isbell and co-worker [8] electrolyzed an aqueous alkaline D-glucose solution containing bromide ions and obtained D-gluconic acid. 2-ketogluconic acid was obtained as by-product.

Electrochemical oxidation to obtain the corresponding acid from D-glucose was also applied by Szwarcz [9], Fink [10], Fioshin and co-workers [11], and Biniecki and Moll [12]. The last-cited authors achieved a yield of 50 to 60%, important also as compared to oxidation with oxidants.

Korotky [13] succeeded to achieve a yield of 86% in the oxidation of D-glucose to D-gluconic acid. He used air as oxidant, and a platinum catalyst on bone black. Experimental conditions were 20 °C; pH 6.0—7.1; 100 g catalyst containing 5% by weight platinum to oxidize 90 g of D-glucose.

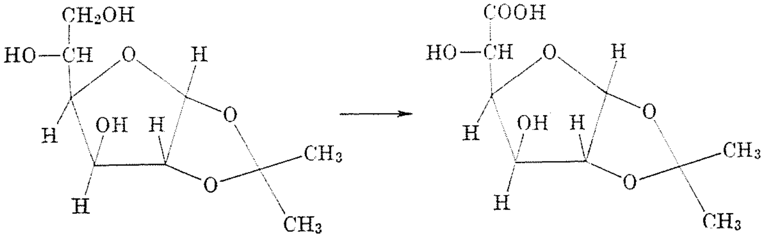
Ion exchange resins in alkaline media are also applied for the oxidation of D-glucose with air to D-gluconic acid. For instance, BONACZEK [14], used the anion-exchange resin Wofatit SBW and achieved a yield of 78%.

PABT and DHAR [15] oxidized D-glucose to D-gluconic acid with air in the presence of an iron oxide catalyst.

BUSCH [16] used palladium catalyst (25% by weight) on calcium carbonate support, at 35 °C in KOH solution.

SEICHI OKUI [17] achieved a conversion of 50% with platinum catalyst, in alkaline solution at 85 °C in the course of 10 hours. Half of the product was D-gluconic acid, while the remainder consisted of oxalic acid, saccharic acid, glyoxylic acid, and tartronic acid.

We prepared MAG from D-glucose as described by MEHLTRETTER and co-workers [5]. MAG contains the furanose ring. As a result of oxidation carried out under appropriate conditions, 1,2-O-*iso*-propylidene-D-glucuronic acid is obtained:



The yield of the oxidation is satisfactory (83%). However, by-products are also formed. Among these, the formation of oxalic acid can readily be followed. In MAG, only the glucosidic hydroxyl and the secondary hydroxyl group next to it are protected. The molecule is liable to oxidation also elsewhere, in addition to the primary hydroxyl group.

We investigated the oxidation of MAG at various temperatures (Fig. 1) and found that the rate of oxidation was maximum around 60 °C (Fig. 2). Apparent activation energy calculated by the Arrhenius equation (Fig. 3) between 40 and 60 °C is 3.3 kcal/mol, i.e. substantially lower than the value measured with di-O-*iso*-propylidene hexoses, viz. 5.5 to 16.0 kcal/mol.

Oxidations carried out with solutions of MAG at different concentration (Fig. 4) demonstrated that the rate of reaction *vs.* concentration (Fig. 5) passed through a minimum. This is the result of maximum rate of oxalic acid formation at this concentration (Fig. 10).

The amount of oxalic acid formed at the oxidation of MAG at various temperatures was also measured (Fig. 6). The rate of oxalic acid formation was found to sharply increase above 70 °C (Fig. 7). The apparent activation

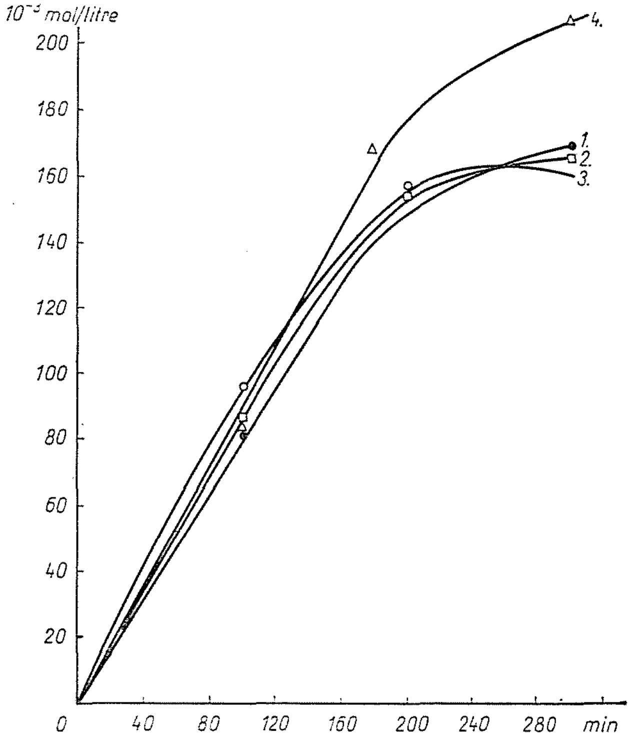


Fig. 1. Oxidation of MAG *vs.* time at different temperatures. 1—45 °C; 2—55 °C; 3—70 °C; 4—85 °C

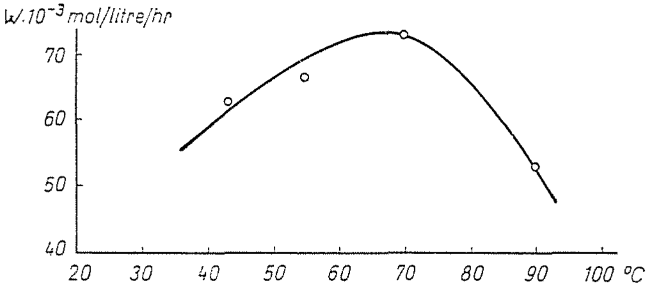


Fig. 2. Rate of MAG oxidation *vs.* temperature

energy of oxalic acid was calculated by the Arrhenius equation (Fig. 8) to 2.6 kcal/mol. Hence, MAG should be oxidized to the corresponding monocarbonic acid at temperatures below 70 °C to obtain less of by-product. We also measured the amount of oxalic acid formed in the oxidation of MAG solutions with different concentrations at 85 °C (Fig. 9). Here the rate of oxalic acid

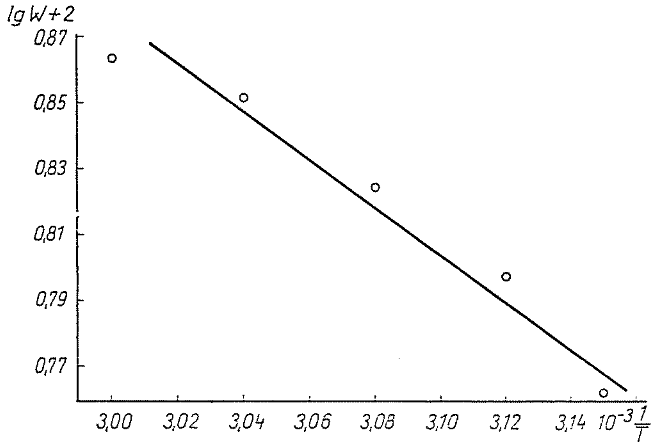
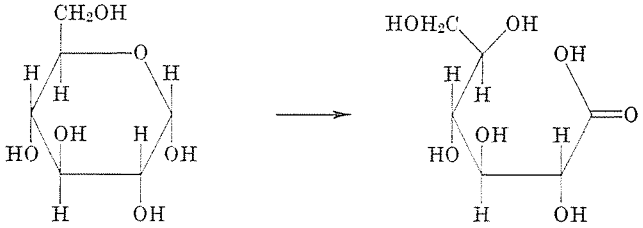


Fig. 3. Logarithm of the rate of MAG oxidation *vs*. 1/T (40 to 60 °C)

formation is already high. The rate of oxalic acid formation *vs*. concentration (Fig. 10) passes through a maximum.

Oxidation of D-glucose under mild conditions yields D-gluconic acid, that is, the carboxyl group is formed by oxidation of the carbonyl group on the first carbon atom:



The glucosidic hydroxyl group being protected, at the oxidation of MAG the carboxyl group will be formed on carbon atom 6 with the primary hydroxyl group.

Oxalic acid is also formed in the oxidation of D-glucose, and even in higher amounts than in the oxidation of MAG. However, by appropriate reaction conditions, oxalic acid formation can be suppressed and a yield of D-gluconic acid close to 90% can be achieved.

Similarly to the oxidation of MAG, maximum rate of oxidation for D-glucose is also found around 60 °C (Figs 11 through 15). Apparent activation energy calculated from the Arrhenius equation for the 43 to 40 °C range amounted to 2.7 kcal/mol (Fig. 16).

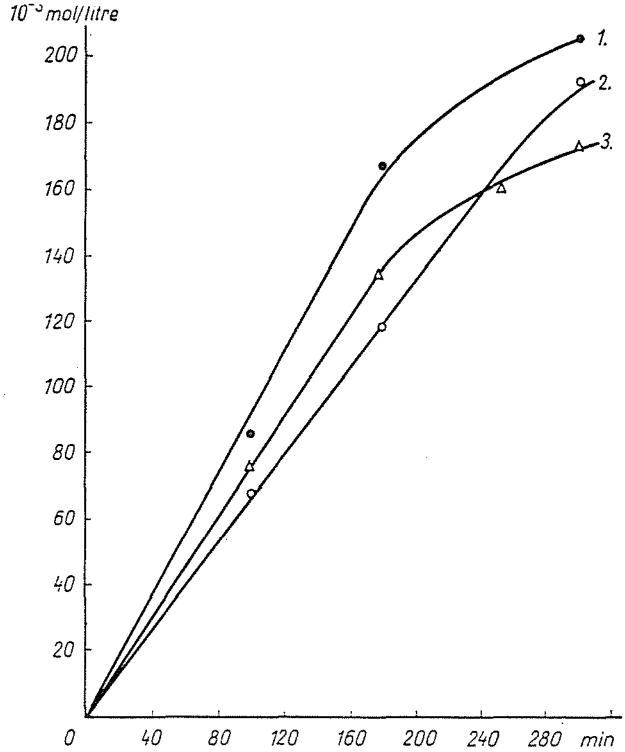


Fig. 4. Oxidation of MAG *vs.* time at different initial concentrations. 1—192.0 · 10^{-3} mol/litre; 2—386.0 · 10^{-3} mol/litre; 3—578 · 10^{-3} mol/litre

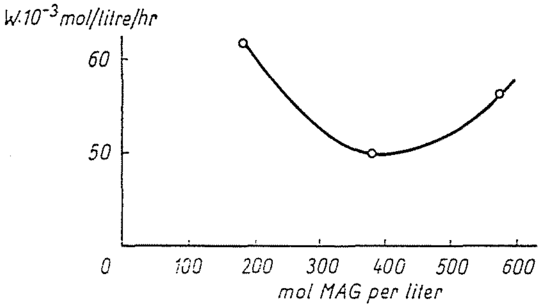


Fig. 5. Rate of MAG oxidation *vs.* concentration (t = 85 °C)

At 60 °C, the rate of reaction increases with concentration up to a defined concentration, and subsequently changes only slightly (Fig. 17). At temperatures lower than 60 °C, the rate of reaction increases proportionally to concentration (Fig. 18).

We also measured the amount of oxalic acid formed at different temperatures and concentrations (Figs 19 through 22). The rate of oxalic acid forma-

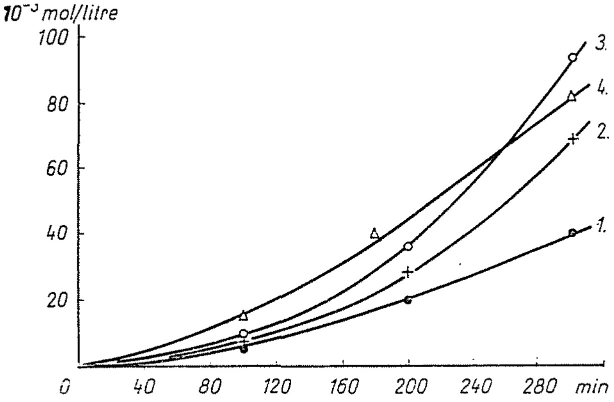


Fig. 6. Oxidation of MAG to oxalic acid *vs.* time at different temperatures. 1 — 45 °C; 2 — 55 °C; 3 — 70 °C; 4 — 85 °C

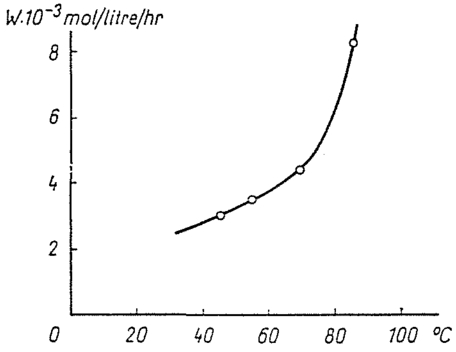


Fig. 7. Rate of MAG oxidation to oxalic acid *vs.* temperature

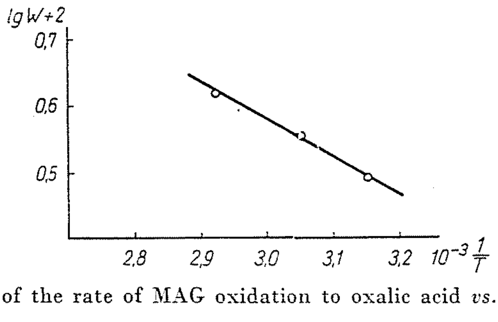


Fig. 8. Logarithm of the rate of MAG oxidation to oxalic acid *vs.* 1/T (45—70 °C)

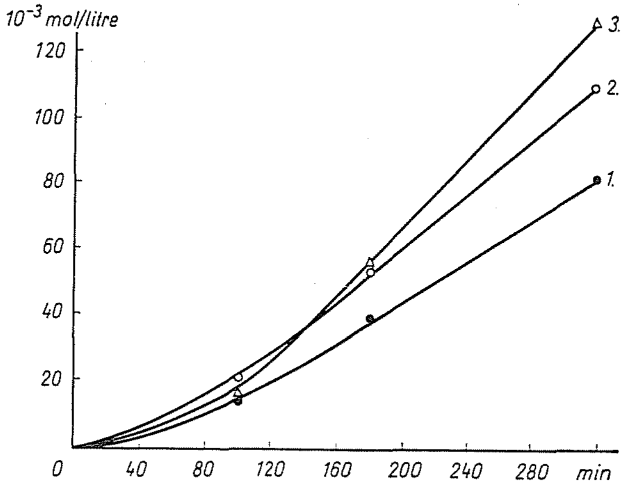


Fig. 9. Oxidation of MAG to oxalic acid *vs.* time, at different initial concentrations of MAG in the solution. 1 — 192.0 · 10^{-3} mol/litre; 2 — 384.0 · 10^{-3} mol/litre; 3 — 576.0 · 10^{-3} mol/litre

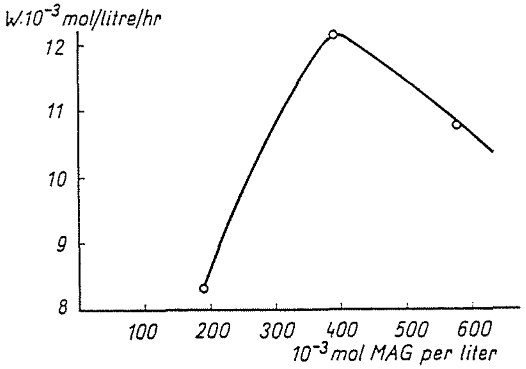
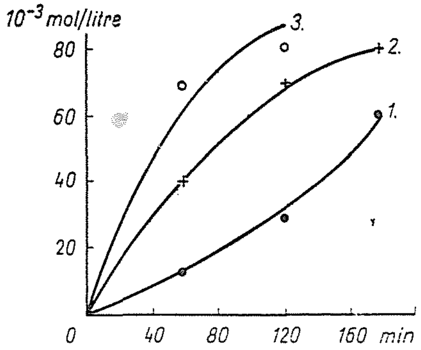


Fig. 10. Rate of MAG oxidation to oxalic acid *vs.* concentration (t = 85 °C)



Figs 11—14. Oxidation of D-glucose to D-gluconic acid *vs.* time at different concentrations and temperatures. 1 — 20 °C; 2 — 40 °C; 3 — 60 °C; 4 — 80 °C. Initial concentration of D-glucose: 138.9 · 10^{-3} mol/litre (Fig. 11); 195.0 · 10^{-3} mol/litre (Fig. 12); 416.7 · 10^{-3} mol/litre (Fig. 13); 555.6 · 10^{-3} mol/litre (Fig. 14)

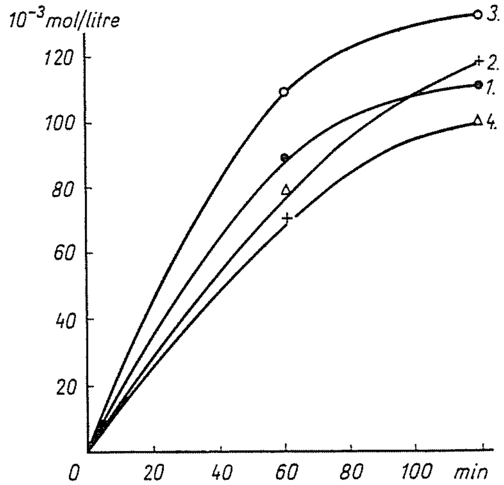

10⁻³ mol/litre
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Fig. 12

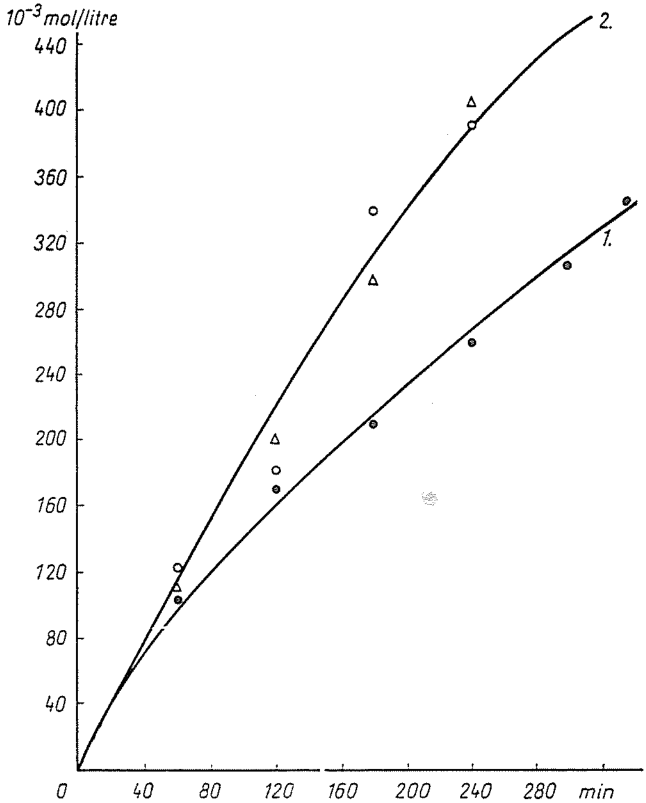
10⁻³ mol/litre
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Fig. 13

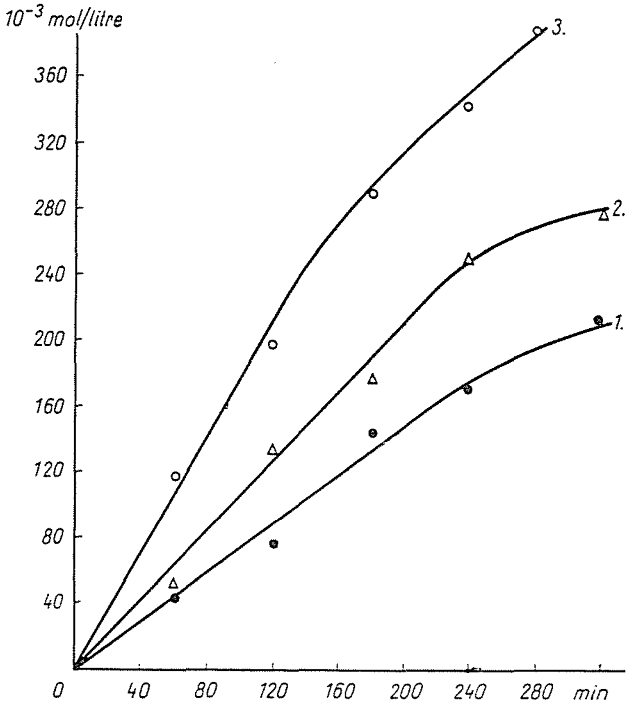


Fig. 14

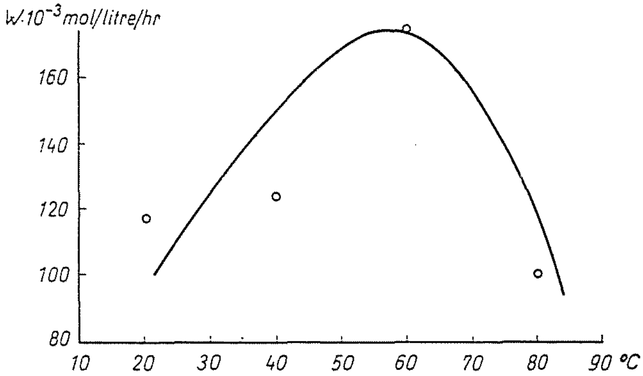


Fig. 15. Rate of D-glucose oxidation to D-gluconic acid *vs.* temperature

tion also passes through a maximum around 40 °C (Fig. 23). From the Arrhenius equation (Fig. 24) the apparent activation energy of oxalic acid formation was found to be 4.5 kcal/mol.

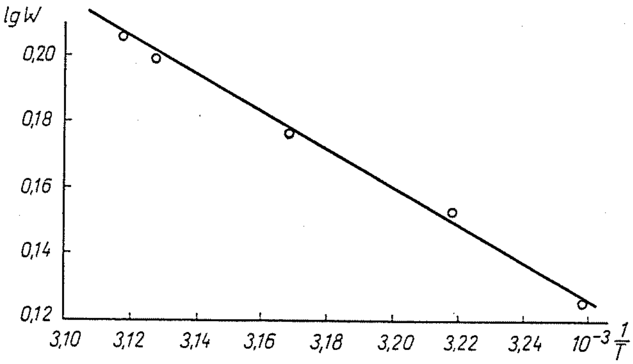


Fig. 16. Logarithm of the rate of D-glucose oxidation to D-gluconic acid *vs.* 1/T (34 to 38 °C)

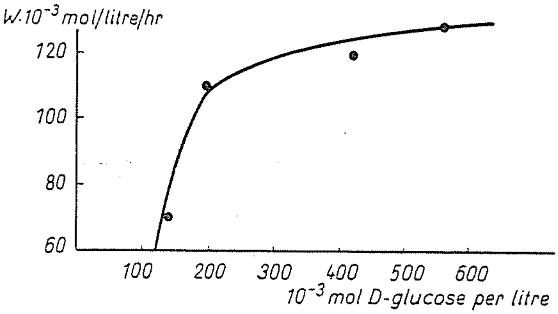


Fig. 17. Rate of D-glucose oxidation to D-gluconic acid *vs.* concenration at 60 °C

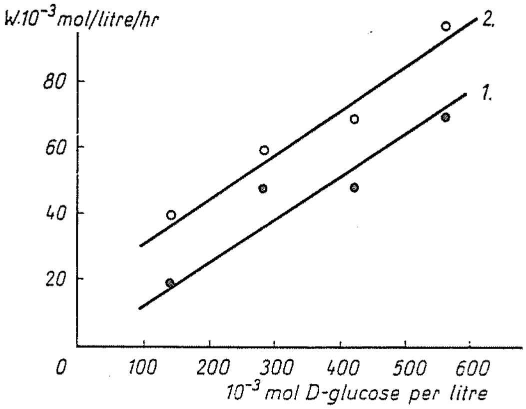
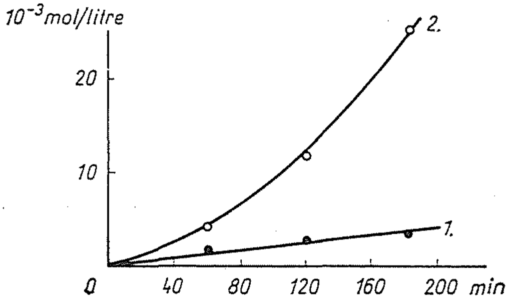


Fig. 18. Rate of D-glucose oxidation to D-gluconic acid *vs.* concentration, at different temperatures 1 — 20 °C; 2 — 40 °C



Figs 19—22. Oxidation of D-glucose to oxalic acid *vs.* time at different concentrations and temperatures 1 — 20 °C; 2— 40 °C; 3 — 60 °C; 4 — 80 °C. Initial concentration of D-glucose: 138.9 · 10^{-3} mol/litre (Fig. 19); 277.8 · 10^{-3} mol/litre (Fig. 20); 416.7 · 10^{-3} mol/litre (Fig. 21); 555.6 · 10^{-3} mol/litre (Fig. 22)

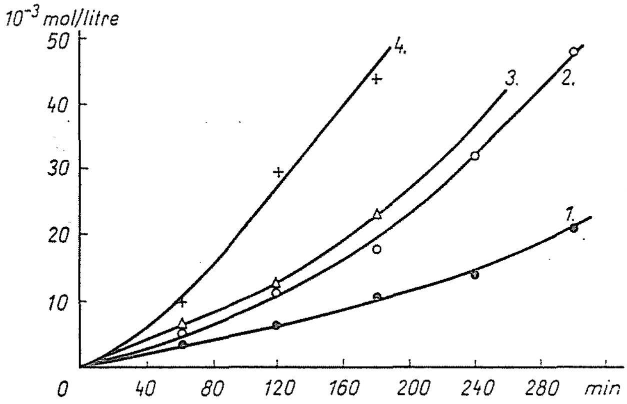


Fig. 20

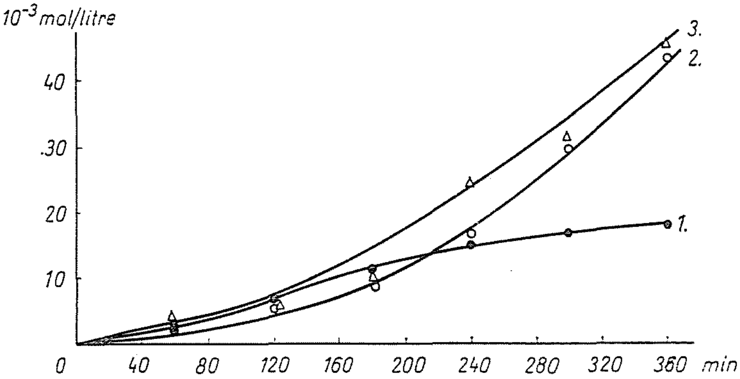


Fig. 21

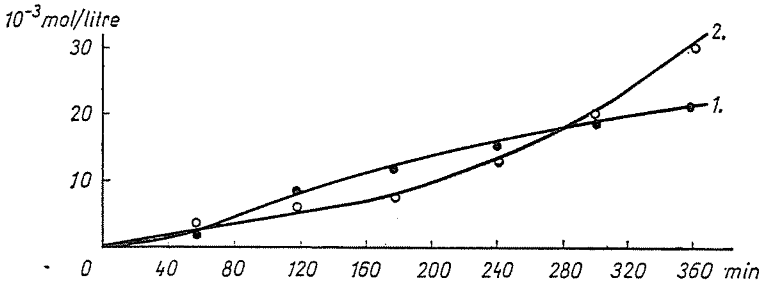


Fig. 22

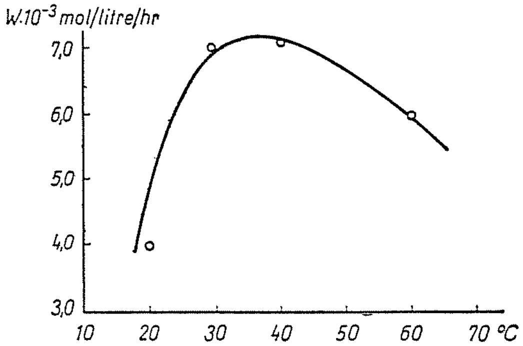


Fig. 23. Rate of D-glucose oxidation to oxalic acid *vs.* temperature

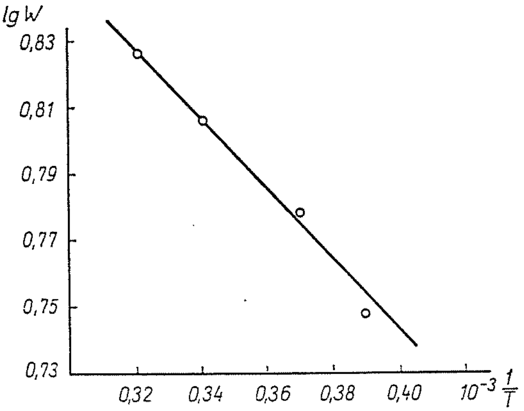


Fig. 24. Logarithm of the rate of D-glucose oxidation to oxalic acid *vs.* 1/T(22 — 28 °C)

The rate of oxalic acid formation *vs.* concentration of D-glucose passes through a maximum (Fig. 25).

It may thus be concluded that to produce D-gluconic acid, it is expedient to carry out oxidation of D-glucose at a temperature below 40 °C and a minimum concentration of $300 \cdot 10^{-3}$ mol glucose per litre.

For a deeper study of the oxidation of D-glucose we investigated the oxidation of D-gluconic acid (Figs 26 through 30).

In these experiments the amount of oxalic acid formed was measured. Under the given conditions, maximum 1 mol of oxalic acid and an acid consuming alkali amounts equivalent to half of the oxalic acid were found to be formed. Presumably oxalic acid and a monocarbonic acid with four carbon atoms formed in the oxidation of D-gluconic acid. Oxidation carried out at different temperatures (Fig. 31) demonstrated the rate of oxidation *vs.* temperature to follow a curve with a maximum around 40 to 50 °C. The apparent activation energy from the Arrhenius plot (Fig. 32) gave a value of 3.0 kcal/mol.

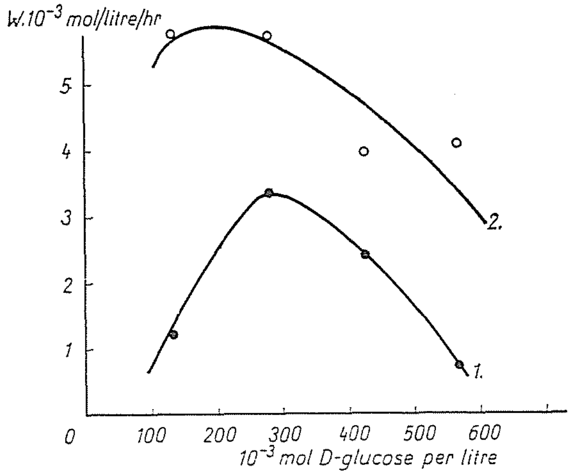
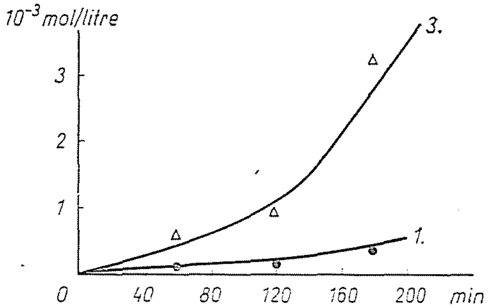


Fig. 25. Rate of D-glucose oxidation to oxalic acid *vs.* concentration at different temperature 1 — 20 °C; 2— 40 °C



Figs 26—30. Oxidation of D-gluconic acid to oxalic acid *vs.* time at different concentrations and temperatures. 1 — 20 °C; 2 — 30 °C; 3 — 40 °C; 4 — 60 °C; 5 — 70 °C; 6 — 90 °C. Initial concentration of D-gluconic acid: 22.9 · 10^{-3} mol/litre (Fig. 26); 69.0 · 10^{-3} mol/litre (Fig. 27); 114.6 · 10^{-3} mol/litre (Fig. 28); 229.0 · 10^{-3} mol/litre (Fig. 29); 344.0 · 10^{-3} mol/litre (Fig. 30)

The rate of oxalic acid formation *vs.* concentration of D-gluconic acid yields a curve similar to the one found for the oxidation of D-glucose (Fig. 33).

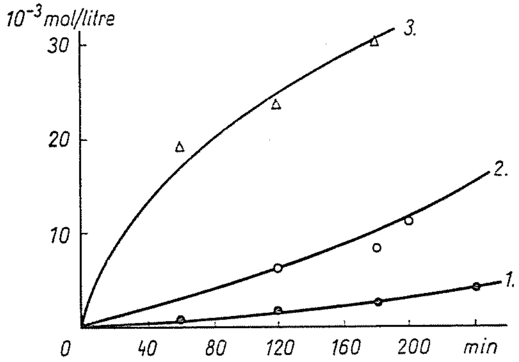


Fig. 27

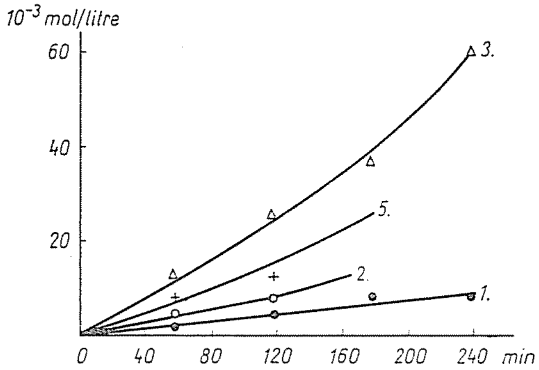


Fig. 28

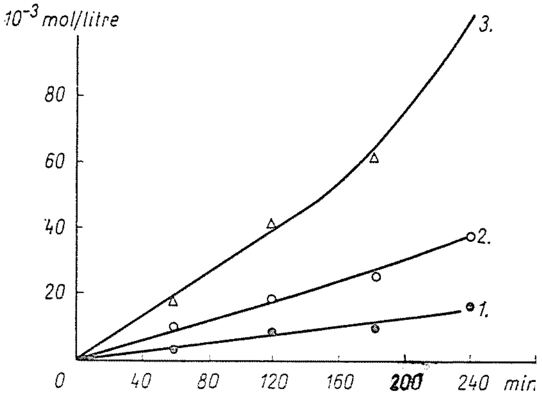


Fig. 29

The formation of the by-product oxalic acid could readily be followed in the oxidation of both MAG and D-glucose. Maximum 1 mol of oxalic acid per mol of substrate was formed, and the total quantity of by-products was found to be proportional to the quantity of oxalic acid. For this reason it appeared of interest to investigate the conditions of oxalic acid formation. It was stated that by-product formation could be suppressed by increasing the initial concentration of the substrate and reducing the temperature of oxidation.

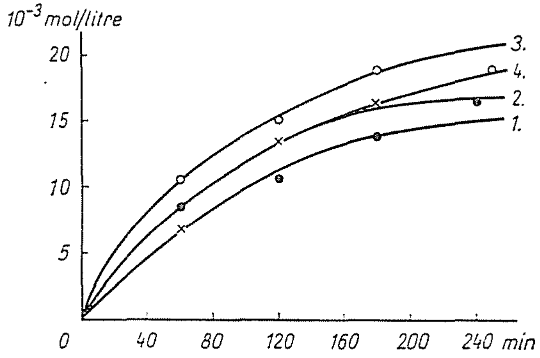
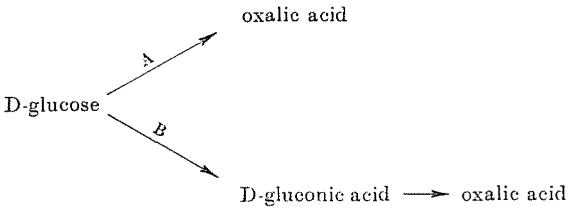


Fig. 30

Under the studied conditions, oxalic acid will not further be oxidized. The desired product in the oxidation of D-glucose is D-gluconic acid. Studies of the oxidation of D-gluconic acid demonstrated that this reaction also yielded oxalic acid in the same proportion as in the case of D-glucose. Thus it appears that, theoretically, oxalic acid can be formed from D-glucose by either



It could be decided unequivocally that path B corresponded to the actual reaction, testified as follows:

(i) We plotted the momentary rate of oxalic acid formation in the course of D-glucose oxidation against the momentary concentration of D-gluconic acid (Fig. 34).

The relationship was found to be linear, indicating that the rate of oxalic acid formation is unequivocally dependent on the concentration of glucon-

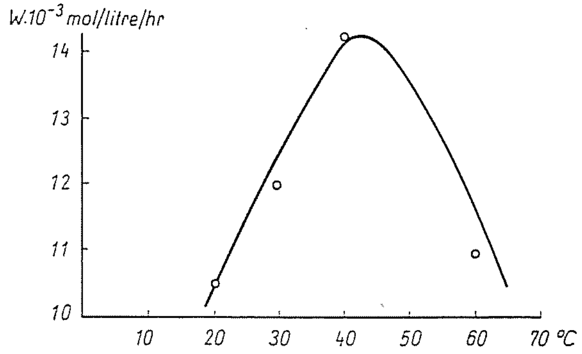


Fig. 31. Rate of D-gluconic acid oxidation to oxalic acid *vs.* temperature

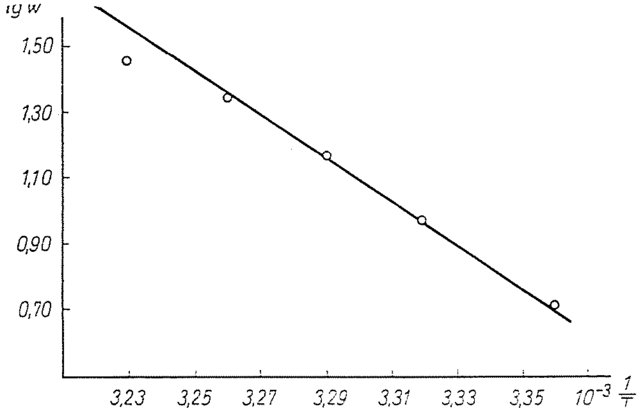


Fig. 32. Logarithm of the rate of D-gluconic acid oxidation to oxalic acid *vs.* 1/T (25—37 °C)

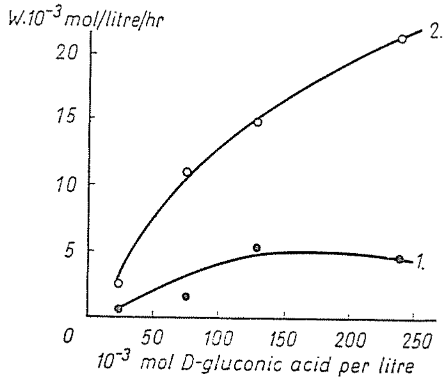


Fig. 33. Rate of D-gluconic acid oxidation to oxalic acid *vs.* concentration at different temperatures 1 — 20 °C; 2 — 40 °C

ic acid, and that the reaction D-gluconic acid → oxalic acid is of the first order.

(ii) We investigated the oxidation of D-gluconic acid in a solution containing no D-glucose. The kinetics of oxalic acid formation were essentially identical with those in the former case (Fig. 35).

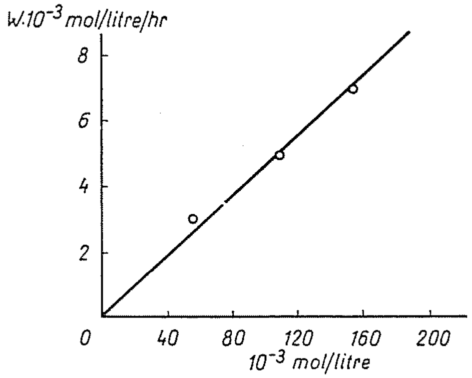


Fig. 34. Momentary rate of oxalic acid formation *vs.* momentary concentration of D-gluconic acid

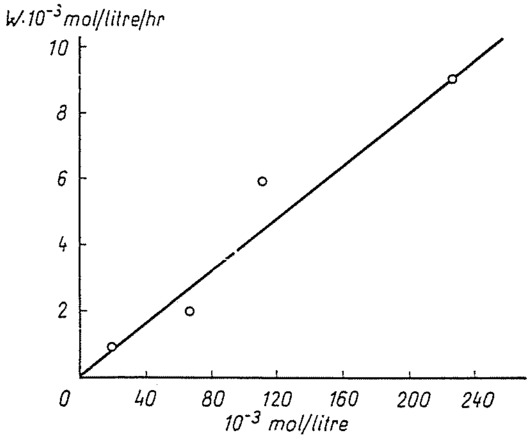


Fig. 35. Initial rate of oxalic acid formation *vs.* initial concentration of D-gluconic acid

Hence, further oxidation of the formed D-gluconic acid and its desorption from the catalyst are competing, parallel processes. D-gluconic acid formed in the oxidation of D-glucose and adsorbed in some form on the surface of the catalyst is likely to be further oxidized to oxalic acid. It may therefore be expected that the formation of oxalic acid in the oxidation of D-glucose will be reduced by all factors promoting desorption of D-gluconic acid. Thus, increased D-glucose concentration will reduce the initial rate of oxalic acid formation, since D-glucose is readier adsorbed and displaces D-gluconic acid (or gluconate ions) from the surface of the catalyst (Fig. 36). FROMAGEOT and WEUMSER [18] investigated the extent of adsorption of various organic acids from their aqueous solutions on the surface of active carbon. They found that the specific adsorption of acids readily adsorbed from acid media was reduced by several orders of magnitude with increasing pH, so that from neutral or slightly alkaline solutions, these compounds would practically not be adsorbed. This is the result of the substantially lower extent of ion adsorption on apolar adsorbents as compared to undissociated molecules [12]. Ash-free active carbon is apolar, and a pure palladium surface can also be regarded apolar. Should oxygen be chemically combined, a slightly basic adsorbent surface results. Anyhow, the presence of OH^- and HCO_3^- ions in the medium will certainly suppress the adsorption of anions of the acid. This is confirmed by our finding that oxidation with air was possible in alkaline solution only. In acid medium the reaction stopped at a conversion of some per cents.

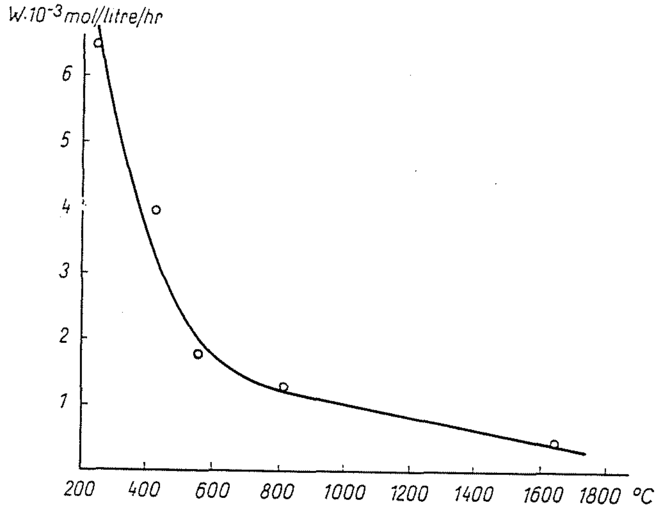


Fig. 36. Momentary rate of oxalic acid formation *vs.* initial concentration of D-glucose

Substantial amounts of oxalic acid are formed in the oxidation of MAG too. The rate of oxalic acid formation depends on MAG concentration in a manner similar to the dependence presented in Fig. 34. Oxalic acid may be assumed to form by further oxidation of the primary oxidation product, namely monoacetone-D-glucuronic acid.

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Summary

Palladium catalysts on bone black support developed earlier by us are well suited for the catalytic oxidation with air of di-0-*iso*-propylidene hexoses in aqueous alkaline medium. We studied the application of these catalysts in the catalytic oxidation with air of 1,2-0-*iso*-propylidene-α-D-glucofuranose and D-glucose. The rate of oxidation plotted against temperature and concentration yields curves passing through a maximum. We stated that the corresponding monocarbonic acid was obtained from these compounds with a yield close to 90%, but only if the concentration of the substrate was high, since in dilute solutions oxidation proceeded further.

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