

CONVERSION OF 2,3:4,6-DI-O-ISOPROPYLIDENE-L-SORBOSE
TO 2,3:4,6-DI-O-ISOPROPYLIDENE-2-KETO-L-GULONIC ACID
BY CATALYTIC OXIDATION WITH OXYGEN ON PLATINUM

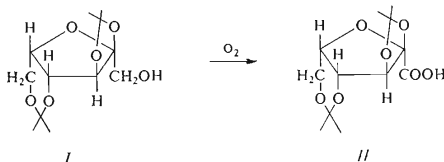
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The kinetics of the oxidation of 2,3:4,6-di-O-isopropylidene-L-sorbose to 2,3:4,6-di-O-isopropylidene-2-keto-L-gulonic acid by oxygen were determined in the aqueous alkaline medium and over platinum on carbon as the catalyst. The most adequate kinetic equation suggested on the basis of non-linear regression was that of the Langmuir-Hinshelwood type. The corresponding most probable reaction mechanism involved an equilibrium single-site adsorption of the substrate, a dissociative dual-site adsorption of oxygen and a surface reaction between oxygen and the substrate to form aldehyde in the rate determining step; in the aqueous alkaline medium the aldehyde is oxidized in the next step to give the anion of 2,3:4,6-di-O-isopropylidene-2-keto-L-gulonic acid. This mechanism appears to be generally applicable to the catalytic transformations of primary alcohols into carboxylic acids by oxygen or air under the above reaction conditions. A linear correlation of the relative reactivities of a series of water-soluble primary aliphatic alcohols with the Taft σ^* constants shows the polar substituent effect to play the predominant role. However, ethanol is approximately twenty times as reactive as 2,3:4,6-di-O-isopropylidene-L-sorbose and this indicates that in the oxidation of the latter compound also strong steric effects should apply.

The oxidation of alcohols by air or oxygen in the presence of platinum has been reported by Strecer¹ in 1855. The ensuing investigations have shown that in the aqueous alkaline medium the primary alcohols are transformed into alkali metal salts of carboxylic acids, while in non-aqueous solutions the aldehydes are the final products; secondary alcohols are oxidized to form the corresponding ketones². The oxidation reactions of primary alcohols include also the transformation of 2,3:4,6-di-O-isopropylidene-L-sorbose (DIS) (*I*) into 2,3:4,6-di-O-isopropylidene-2-keto-L-gulonic acid (DKG) (*II*) (Scheme 1), which constitutes one step in the well-known



SCHEME 1

Reichstein synthesis of ascorbic acid. The industrial process based on the oxidation of DIS with sodium hypochlorite brought about some environmental and economical problems and other methods of oxidation were therefore sought to improve the process parameters. There exist only a few informations in the literature on the catalytic oxidation of DIS by air or oxygen; two patents claim the use of platinum and palladium as catalysts^{3,4}.

A detailed mechanism of the catalytic transformation of alcohols into carboxylic acids by oxygen in the presence of platinum metals is still unclear. Various mechanistic schemes were suggested including a heterogeneous catalytic oxidation and oxidative dehydrogenation or even a radical reaction initiated by the catalyst surface and proceeding then in the homogeneous phase⁵⁻⁸. Most recently, Dirx and van der Baan⁹ have reported the oxidation of gluconic acid on the Pt/C catalysts to yield glucaric acid as the final product. The formation of the aldehydic intermediate, guluronic acid, was found to be the slowest step; oxidation of this intermediate proceeded faster than that of the hydroxymethyl group in gluconic acid. The catalyst deactivation has been explained as due to the formation of Pt—O and PtO₂ species on the catalyst surface.

In order to gain a deeper insight into the mechanism of the catalytic oxidation of DIS with oxygen, we have measured the initial rates of this reaction in the aqueous alkaline medium and in the presence of 2% of platinum on carbon as the catalyst. The study includes the catalytic oxidation of several water-soluble primary aliphatic alcohols and determination of their relative reactivities. An attempt is made to correlate these reactivities with the Taft σ^* and E_s constants. The results are used to suggest the most adequate reaction scheme for the catalytic transformation of DIS into DKG on platinum metals in aqueous alkaline solutions, which could be generally valid for the oxidations of primary alcohols by air or oxygen on these catalysts.

EXPERIMENTAL

Chemicals. DIS (m.p. 76–78°C) was obtained by crystallization of the technical product (Farmakon, Olomouc) from light petroleum–toluene (2 : 1). DKG used as the standard for liquid chromatography was purified by repeated crystallizations of the technical monohydrate (Farmakon, Olomouc) from acetone; the pure product had m.p. 93–94°C. Methanol, ethanol, n-propanol, n-butanol, isobutanol and 2-methoxyethanol, all reagent grade chemicals (Lachema, Brno), were dried over molecular sieves and distilled. Reagent grade acetone, formaldehyde (aqueous 36–38% solution), sodium hydroxide and sodium carbonate (Lachema, Brno) were used as obtained. Chloroplatinic acid hexahydrate was purchased from Safina (Vestec).

Catalyst preparation. Granules of carbon GA-1 (Slovak Chemical Works, Hnúšťa) suspended in 20% nitric acid were warmed to boiling, washed with distilled water, dried, ground and sieved to a particle size of 0.03–0.1 mm. The carbon fraction (98 g) suspended in distilled water (400 ml) was warmed to boiling and to the stirred suspension was added 50 ml of 1M hydrochloric acid which contained chloroplatinic acid hexahydrate in an amount (5.309 g) corresponding to 2 g of platinum. After stirring for 30 min, 20 ml of a 20% sodium hydroxide solution and 20 ml of aqueous formaldehyde were added dropwise. The stirred mixture was warmed to boiling for 1 h and stirring was continued for 30 min. The cooled suspension was filtered and the catalyst was washed with 50 ml of distilled water, dried in air at 20°C and stored in an exsiccator over activated silica gel.

Apparatus. The main part of the apparatus was a cylindrical glass reactor with 90 mm in diameter and 180 mm high equipped with a thermometer, a reflux condenser and a nitrogen or oxygen inlet. The actual reactor volume was about 250 ml. Four vertical stainless-steel baffles were placed symmetrically in the lower part of the reactor. The gas was dispersed in the reaction mixture by means of a centrifugal stirrer which consisted of a hollow teflon cone 60 mm high and having at the base 50 mm in diameter; gas dispersion was enhanced by placing symmetrically eight 1 mm holes at the cone base. The stirring was regulated in the range 1 000–4 000 revs/min. The partial pressure of oxygen in the gas phase was adjusted by means of conventional regulation valves. As the flow of oxygen was about ten times as high as the supposed oxygen consumption, the composition of the gas phase was assumed to be constant throughout a measurement. The temperature of the reaction mixture was kept constant within $\pm 1^\circ\text{C}$.

Kinetic measurements. The reactor containing 200 ml of a sodium carbonate solution ($0.5 \text{ mol} \cdot \text{l}^{-1}$) and weighed amounts of the catalyst and DIS was flushed with nitrogen and the mixture was allowed to warm under stirring to the desired temperature. Next, the zero sample of the reaction mixture was transferred from the reactor and the desired partial pressure of oxygen was adjusted. In order to avoid entrainment of the substrate, the flow of oxygen was adjusted so as to maintain a flow rate equal to 1 ml min^{-1} at the reactor outlet. The same procedure was used for determining the initial rates of oxidation of primary alcohols. Parallel experiments have shown that the rate of oxidation does not change with the intensity of stirring in the range from 2 000 to 4 000 revs./min. By using the Mears criteria¹⁰ it was proved that the reactions proceeded with respect to oxygen in the kinetic region¹¹. As the reactions were nearly zeroth order in DIS, the reaction rates could not be influenced by the DIS transport. The concentrations of DIS varied between 0.1 and 0.5 mol l^{-1} . The upper concentration limit is given by the limited solubility of DIS in the aqueous sodium carbonate solution and the lower limit by the sensitivity and accuracy of the reversed-phase liquid chromatography used as the analytical method. According to the Henry's law, the concentration of oxygen in the liquid phase (c_{O_x}) was equal to its partial pressure in the gas phase (p_{O_x}). Since the corresponding Henry's constant is not known, p_{O_x} is used in place of c_{O_x} throughout all calculations.

Analytical methods. Transformation of DIS into DKG was followed by the reversed-phase liquid chromatography. The advantage of this technique lies in the simple pretreatment of a sample involving only separation of the catalyst by filtering an aliquot of the reaction mixture. Analyses were carried out by using a liquid chromatograph consisting of a high-pressure pump VC 300 (Development Workshops, Prague), a six-port sampling valve, a pulse damper and a differential refractometer RD 1 (Development Workshops, Prague). The column ($2.5 \text{ m} \times 4 \text{ mm}$) was packed with Separon SI C18 ($10 \mu\text{m}$) (Laboratory Instruments, Prague). Aqueous methanol solution (30% v/v) containing 0.01% of tetrabutylammonium chloride was used as the mobile phase at a flow rate of 1.5 ml min^{-1} ; the pressure at the column outlet was 9.5 MPa. Samples from the oxidation of lower aliphatic alcohols were analysed by gas chromatography on the Chrom 3 apparatus (Laboratory Instruments, Prague) equipped with a flame-ionization detector and a stainless-steel column ($3 \text{ m} \times 3 \text{ mm}$), which was packed with 8% Reoplex on Chromaton N-AW; the column temperature was $120\text{--}140^\circ\text{C}$. Analyses of samples from the oxidation of methanol were carried out on a column ($2 \text{ m} \times 3 \text{ mm}$) packed with 4% propylene glycol–12% dinonyl sebacate on Celite; column temperature was 75°C .

RESULTS AND DISCUSSION

The conversion of DIS as a function of time (Fig. 1) documents that a portion of DIS reacts already in the nitrogen atmosphere, evidently by virtue of the interac-

tion with oxygen chemisorbed on the catalyst surface. From these experiments it further follows that the initial reaction rate of oxidation of DIS (r_0) related to a unit weight of the Pt/C catalyst does not depend on the catalyst concentration (c_{cat}):

$c_{\text{cat}}, \text{g l}^{-1}$	7.5	15	30	40
$r_0 \cdot 10^4, \text{mol kg}^{-1} \text{s}^{-1}$	3.33	3.63	2.92	3.06

The oxidation of DIS on the Pt/C catalyst therefore appears to be a typical heterogeneous catalytic reaction and a radical oxidation of DIS in the heterogeneous phase^{7,8} can thus be excluded from further considerations.

Fig. 2 shows the dependence of the initial rate of oxidation of DIS (r_0) upon the partial pressure of oxygen (p_{O_2}) and the concentration of DIS (c_A), the latter varying between 0.1 and 0.5 mol l⁻¹. By applying the empirical power rate equation $r_0 = kc_A^n p_{\text{O}_2}^m$ we have found that the oxidation reaction is essentially zeroth order in DIS ($n = 0.02$) and approximately one-half order in oxygen ($m = 0.41$).

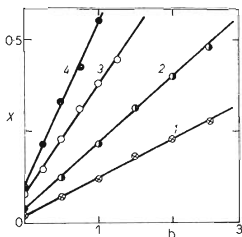


FIG. 1

Time dependence of the conversion of DIS (X) upon concentration of the Pt/C catalyst. [Pt/C]: 1 7.5 g l⁻¹, 2 15 g l⁻¹, 3 30 g l⁻¹, 4 40 g l⁻¹; [DIS]₀ = 0.1 mol l⁻¹; p_{O_2} = = 0.02 MPa; temperature 100°C

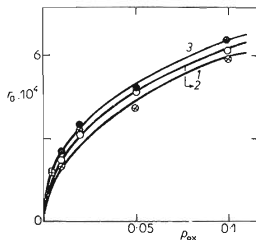


FIG. 2

Initial rates of oxidation of DIS (r_0) (mol . kg⁻¹ s⁻¹) as a function of the partial pressure of oxygen (p_{O_2}) (MPa) and the concentration of DIS (c_A). [DIS]₀: 1 0.1 mol . l⁻¹, 2 0.2 mol l⁻¹, 3 0.5 mol l⁻¹; [Pt/C] = = 25 g l⁻¹; temperature 100°C

TABLE I

Kinetic models, the corresponding kinetic equations, correlation coefficients (r), rate (k_i) and equilibrium constants (K_i), sums of squares of deviations (Q_i) and "maximum likelihood ratio" (L_{\max}) for the oxidation of DIS (A) by oxygen over the Pt/C catalyst

No Model/ equation	Kinetic model	Kinetic equation	Constants	$Q_i \cdot 10^8$	L_{\max}	r
(1)	$\text{O}_2 + 2\text{L} \xrightleftharpoons{K_{\text{O}_2}} 2\text{OL}$ $\text{A} + \text{L} \xrightleftharpoons{K_{\text{A}}} \text{AL}$ $\text{AL} + \text{OL} \xrightarrow{k} 2\text{L} + \text{prod.}$	$r_0 = \frac{k K_{\text{A}} C_{\text{A}} (K_{\text{O}_2} P_{\text{O}_2})^{0.5}}{[1 + K_{\text{A}} C_{\text{A}} + (K_{\text{O}_2} P_{\text{O}_2})^{0.5}]^2}$	$k = 1.12 \cdot 10^{-2} \text{ a}$ $K_{\text{A}} = 4.86 \text{ b}$ $K_{\text{O}_2} = 1.01 \text{ c}$	1.26	—	0.9949
(2)	$\text{O}_2 + \text{L} \xrightleftharpoons{K_{\text{O}_2}} \text{O}_2\text{L}$ $\text{A} + \text{L} \xrightleftharpoons{K_{\text{A}}} \text{AL}$ $\text{O}_2\text{L} + \text{AL} \xrightarrow{k} 2\text{L} + \text{prod.}$	$r_0 = \frac{k K_{\text{A}} K_{\text{O}_2} C_{\text{A}} P_{\text{O}_2}}{(1 + K_{\text{A}} C_{\text{A}} + K_{\text{O}_2} P_{\text{O}_2})^2}$	$k = 3.63 \cdot 10^{-3} \text{ a}$ $K_{\text{A}} = 1.00 \cdot 10^1 \text{ b}$ $K_{\text{O}_2} = 3.14 \cdot 10^1 \text{ c}$	5.51	$3.06 \cdot 10^4$	0.9090
(3)	$\text{A} + \text{L} \xrightleftharpoons{K_{\text{A}}} \text{AL}$ $\text{O}_2 + 2\text{L} \xrightarrow{k_1} 2\text{OL}$ $\text{AL} + \text{OL} \xrightarrow{k_2} 2\text{L} + \text{prod.}$	$r_0 = \frac{k_1 k_2^2 K_{\text{A}}^2 C_{\text{A}}^2 P_{\text{O}_2}}{(k_2 K_{\text{A}} C_{\text{A}} + k_1 P_{\text{O}_2} + k_2 K_{\text{A}} C_{\text{A}}^2)^2}$	$k_1 = 3.15 \cdot 10^{-2} \text{ d}$ $k_2 = 1.31 \cdot 10^{-2} \text{ a}$ $K_{\text{A}} = 1.55 \text{ b}$	11.13	$4.20 \cdot 10^6$	0.9013

^a Mol kg⁻¹ s⁻¹; ^b l mol⁻¹; ^c MPa⁻¹; ^d mol kg⁻¹ s⁻¹ MPa⁻¹.

In an effort to interpret the given dependences of r_0 upon p_{O_2} and c_A we have derived a series of kinetic equations of the Langmuir–Hinshelwood and redox type; the latter have been used in several cases for description of the kinetics of heterogeneous catalytic oxidation reactions^{12,13}. Linear regression of the experimental data gave three kinetic equations characterized by the largest values of the correlation coefficients; the validity of these equations was proved further by non-linear regression. A combination of equilibrium and rate constants corresponding to the least sum of squares of deviations was found by using the optimization procedure suggested by Marquardt^{14,15}. The kinetic models 1–3, the corresponding kinetic equations (1)–(3), their correlation coefficients, the values of the rate and equilibrium constants and the sums of squares of deviations are summarized in Table I.

For discrimination among the rival kinetic models we have chosen the "likelihood ratio approach"¹⁶. The value of L_{\max} as defined by Eq. (4)

$$L_{\max} = (Q_i/Q_1)^{n/2} \quad (4)$$

determines the ratio of probabilities with which both rival models describe an experimental dependence. In Eq. (4) Q_1 denotes the sum of squares of deviations obtained for the best kinetic model, Q_i the sums of squares of deviations found for other models ($Q_i > Q_1$) and n is the number of measurements. If L_{\max} attains a sufficiently large value (≥ 100), then the best model can be taken as the most adequate one¹⁶.

From the values of L_{\max} listed in Table I it is evident that a significantly most adequate description of the DIS oxidation is given by the model of the Langmuir–Hinshelwood type (Eq. (1)); this model supposes that the surface reaction between

TABLE II

Relative reactivities (r_{rel}) of primary alcohols in the oxidation by oxygen over the Pt/C catalyst at 50°C and the corresponding Taft E_s and σ^* constants

Alcohol	r_{rel}^a	E_s	σ^*
DIS	~0.05	—	—
2-Methoxyethanol	0.50	-0.19	0.520
Methanol	0.59	1.24	0.490
Ethanol	1.00	0.00	0.000
n-Propanol	1.20	-0.07	-0.100
n-Butanol	1.22	-0.36	-0.115
Isobutanol	1.38	-0.47	-0.190

^a In relation to ethanol.

the adsorbed DIS molecule and the dissociatively adsorbed oxygen is the rate determining step.

The measurement of r_0 as a function of c_A in the oxidation of n-butanol by oxygen on the Pt/C catalyst revealed the reaction to be surprisingly second order in n-butanol (Fig. 3). We believe that the second-order kinetics observed in this case can be explained in terms of Eq. (3). The corresponding reaction model for the catalytic oxidation of n-butanol differs from that suggested for the oxidation of DIS only in the relative rate of oxygen adsorption; if the surface reaction between DIS and oxygen is relatively fast, the adsorption equilibrium of oxygen cannot establish itself rapidly enough and the mechanism of the Langmuir-Hinshelwood type changes

TABLE III

Parameters of the Taft equations and their correlation coefficients (r)

Correlation equations	Parameters δ and ρ	r
$\log r_{rel} = \delta E_s + \text{const.}$	$\delta = -0.041$	0.6035
$\log r_{rel} = \rho \sigma^* + \text{const.}$	$\rho = -0.536^a$	0.9909
$\log r_{rel} = \rho \sigma^* + \delta E_s + \text{const.}$	$\rho = -0.578^b$	0.9971
	$\delta = 0.019$	

^a Const. = 0.022; ^b const. = 0.021.

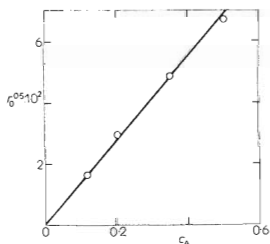


FIG. 3

Linearized dependence of the initial rate of oxidation of n-butanol (r_0) ($\text{mol}^{0.5} \cdot \text{kg}^{-0.5} \text{s}^{-0.5}$) on its concentration (c_A) (mol l^{-1}). $[\text{Pt/C}] = 10 \text{ g l}^{-1}$; $p_{O_2} = 0.1 \text{ MPa}$; temperature 50°C

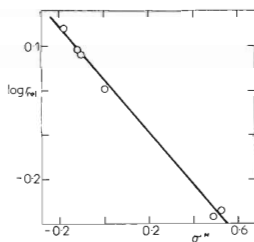


FIG. 4

Linear correlation of the logarithms of relative reactivity (r_{rel}) of primary alcohols (A) (Table III) with the Taft polar constants σ^* . $[c_A]_0 = 0.35 \text{ mol l}^{-1}$; $[\text{Pt/C}] = 25 \text{ g} \cdot \text{l}^{-1}$; $p_{O_2} = 0.1 \text{ MPa}$; temperature 50°C

over to that of the redox type. This conclusion is supported by the fact that the oxidation of n-butanol is about 24 times as fast as that of DIS. The models leading to Eqs (1) and (3) represent extreme cases of a single fundamental mechanism involving an equilibrium single-site adsorption of an alcohol, a dissociative dual-site adsorption of oxygen and a surface reaction of the both adsorbed components to form an aldehyde as the intermediate product in the rate determining step. Traces of butyraldehyde were detected by gas chromatography in the product of oxidation of n-butanol. However, an attempt to find an analogous product also in the oxidation of DIS failed. Nevertheless, the study of oxidation of a hydroxymethyl group in gluconic acid had shown that the reaction proceeds by way of an aldehydic intermediate, *i.e.* guluronic acid⁹. We therefore believe that the absence of an aldehyde in the product of oxidation of DIS was caused merely by the insufficient sensitivity of the analytical method and that the oxidations of primary alcohols over platinum metals and in the aqueous alkaline medium generally proceed *via* the corresponding aldehydes which are rapidly oxidized to anions of the corresponding carboxylic acids.

In order to explain the great difference in reactivity between DIS and n-butanol, we have determined the relative reactivities of several water-soluble primary alcohols by using the method of competitive reactions (Table II). The relative reactivities thus obtained were then correlated with the Taft σ^* and E_s constants. As shown in Table II, the reactivity of primary alcohols increases in the order: 2-methoxyethanol < methanol < ethanol < n-propanol < n-butanol < isobutanol; this is at variance with the observations of Heyns and Blazejewicz², who have found that the reactivity of primary alcohols in the oxidation over Pt/C catalysts and in aqueous alkaline solutions decreases with the increasing length of the carbon chain. However, these experiments were carried out at various temperatures and concentrations, the results could be influenced by different solubility of primary alcohols in water and were therefore not mutually comparable.

Provided that the carbon atom of the hydroxymethyl group is the reaction center, the data in Table III and the linear correlation ($r = 0.9909$) presented in Fig. 4 give evidence that the reactivity of primary alcohols is influenced predominantly by the polar substituent effect. The negative sign of the parameter ρ in the Taft equation (Table III) leads us to conclude that the hydrogen atom is abstracted as a hydride ion in the rate determining step. The relatively low reactivity of DIS (Table II) can be explained as due to the polar effect of the three oxygen atoms occurring in the proximity of the reaction center (Scheme 1). The lower reactivity of 2-methoxyethanol relative to ethanol can be attributed presumably to an analogous effect exerted by the ether oxygen. In the case of DIS, however, we cannot ignore the steric effects which could be evoked by the remaining bulky monosaccharide molecule.

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