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Selective oxidation of methyl α-D-glucoside on carbon supported platinum

II. Assessment of the Arrhenius and Langmuir parameters

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Abstract

In order to estimate the Arrhenius and Langmuir parameters of the selective oxidation of methyl α-D-glucoside on a platinum catalyst, the temperature was varied from 293 to 333 K. The initial reaction kinetics can be described adequately over this temperature range by a Langmuir–Hinshelwood rate equation which is based on two parallel reaction paths: one involving adsorbed methyl α-D-glucoside and dominating at low pH, the other involving the adsorbed methyl α-D-glucoside anion and dominating at high pH. Both reaction paths contain a rate-determining step consisting of a surface reaction involving the corresponding methyl α-D-glucoside species and chemisorbed oxygen. The apparent activation energies amount to 50.5 ± 6.4 kJ mol^{-1} and 110.5 ± 10.6 kJ mol^{-1}. The assessment of the Arrhenius parameter estimates within the framework of the transition state theory showed that these rate-determining steps lead to physically meaningful estimates. Langmuir adsorption coefficients account for the reversible dissociative chemisorption of oxygen and for the reversible associative adsorption of methyl α-D-glucoside and methyl α-D-glucoside anion. A standard adsorption enthalpy for oxygen of -60.0 ± 10.5 kJ mol^{-1}, for methyl α-D-glucoside of -17.6 ± 8.3 kJ mol^{-1} and for the methyl α-D-glucoside anion of -61 ± 54 kJ mol^{-1} were estimated. During the oxidation at a pH of eight oxygen adatoms are the most abundant surface species, followed by adsorbed methyl α-D-glucoside. With increasing temperature the degree of oxygen coverage decreases from 0.8 to 0.6, while the degree of coverage with methyl α-D-glucoside increases from 0.08 to 0.13. At a pH of 10 the surface coverage with oxygen decreases from 0.6 at 293 K to 0.5 at 333 K and the surface coverage with methyl α-D-glucoside anion from 0.5 to 0.3.

Keywords: glucoside, kinetics, oxidation, platinum.

INTRODUCTION

The interest in processes with carbohydrates as chemical feedstock is growing considerably [1]. A first step towards valuable chemicals from carbohy-

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drates may consist of the selective oxidation [2] of one of the functional groups, in particular the primary hydroxyl group.

A variety of techniques is available for the oxidation of the primary alcohol function in carbohydrates [3–6]. Of these, the catalytic oxidation by molecular oxygen on supported platinum is one of the most attractive [7–9]. High selectivities are obtained by using this route. The reaction is carried out in water at temperatures between 293 and 353 K and atmospheric pressure. Heyns and Paulsen [7] reviewed the platinum catalyzed selective oxidation of monosaccharides with molecular oxygen. They concluded that the order of reactivity of the functional groups towards oxygen is as follows: hemi-acetal > primary hydroxyl > axial hydroxyl > equatorial hydroxyl. Hence, in order to oxidize selectively the primary hydroxyl function a protection of the hemi-acetal function is generally required. The present study deals with the platinum-catalyzed oxidation of methyl α-D-glucoside (methyl α-D-glucopyranoside) to sodium 1-O-methyl α-D-glucuronate with molecular oxygen. The stoichiometry of the reaction is shown in Fig. 1.

The platinum catalyzed selective oxidation of methyl α-D-glucoside has hardly been studied [10–12]. Although a number of papers deal with the oxidation of primary alcohols, the detailed reaction sequence is not established and there is a lack of quantitative kinetic studies. In a previous paper it was shown that some insight into the reaction sequence could be obtained by a regression analysis of intrinsic kinetic data obtained in the absence of catalyst deactivation [13]. At 303 K the initial reaction kinetics could be described adequately over a broad range of reaction conditions by a relatively simple rate equation of the Langmuir–Hinshelwood type. The oxidation occurs along two parallel reaction paths: one involving adsorbed methyl α-D-glucoside and dominating at low pH, the other involving the adsorbed methyl α-D-glucoside anion and dominating at high pH. Both reaction paths contain a rate-determining step consisting of a surface reaction between the methyl α-D-glucoside species and chemisorbed oxygen. Furthermore, the rate equation contained Langmuir adsorption terms accounting for the reversible dissociative chemisorption of oxygen and for the reversible associative adsorption of methyl α-
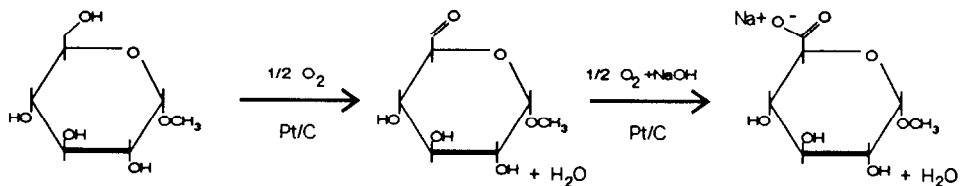

Fig. 1. The oxidation of methyl α-D-glucoside via 1-O-methyl α-D-aldehydo-glucoside to sodium 1-O-methyl α-D-glucuronate [13].

D-glucoside and methyl α-D-glucoside anion. No distinction was made between the sites of chemisorption for oxygen and the methyl α-D-glucoside species.

The ambiguity of steady-state kinetics [14] did not allow us to arrive at more specific conclusions about the reaction mechanism and in particular about the rate-determining step. Nevertheless the validity of the proposed sequences can be further corroborated by verifying whether the rate equation can adequately describe the reaction kinetics over a broad range of temperatures and, if so, whether the corresponding estimates of the Arrhenius and Langmuir parameters are meaningful. The present paper reports on such an analysis.

EXPERIMENTAL

Equipment, procedure and conditions

The experimental set-up and procedure have been described previously [13]. Before an experiment was started at a given temperature, the oxygen electrode and the pH electrode were calibrated at this temperature. The temperature dependence of the oxygen solubility is described according to the correlation for the Henry coefficient given by Fernandez-Prini and Crovetto [15].

The investigated range of reaction conditions is listed in Table 1. In this conversion range sodium 1-O-methyl α-D-glucuronate was obtained with a selectivity of 100%. The reaction conditions were chosen such that the initial reaction rates were free from mass and heat transfer even at the highest temperature. A total of 64 initial reation rates were collected. The reported degrees of coverage of the platinum surface are calculated at the following conditions: $C_{RCH_2OH} = 200$ mol m^{-3}, $p_{O_2} = 1.0 \times 10^5$ Pa, $T = 303$ K, $X = 0.06$.

Catalyst

The catalyst used throughout this kinetic study was a commercial 5.0 wt-% platinum on activated carbon (Degussa F196 RA/W). The fraction of platinum atoms exposed was 0.59, as determined by carbon monoxide-pulse chem-

TABLE 1

Investigated range of reaction conditions

Me.-glucoside concentration (kmol m^{-3})	0.05-1.0
Oxygen partial pressure (Pa)	$5.0 \times 10^3 - 1.0 \times 10^5$
pH	6-10
Catalyst concentration (kg m^{-3})	1-5
Temperature (K)	293-333
Conversion of Me.-glucoside	0.02-0.10

isorption with the assumption of 1:1 stoichiometry. The corresponding platinum surface area amounted to 6.5×10^3 m^2 kg$_{cat}^{-1}$, calculated under the assumption of 1.4×10^{19} platinum atoms m^{-2} [16]. Transmission electron microscopy showed an average platinum particle size of $d_s = 2.20$ and a standard deviation of 1 nm. For this catalyst a specific reaction rate of 1×10^{-3} mol kg$_{cat}^{-1}$ s^{-1} corresponds to a turnover frequency of 0.7×10^{-2} s^{-1}.

The BET surface area amounted to 8.5×10^5 m^2 kg$_{cat}^{-1}$. The catalyst was crushed in a ball mill to reduce the particle diameter from 100 μm maximum to less than 20 μm in order to avoid transport limitations.

Parameter estimation and model discrimination

The data analysis was performed as outlined by Froment and Hosten [17]. To facilitate the estimation of activation energies and standard adsorption enthalpies a reparametrization was applied (cf. Notation):

$$k = A^0 \exp\left(-\frac{E^a}{RT} \right) = A^{0\prime} \exp\left[\frac{E^a}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \tag{1}$$

$$K = \exp\left(\frac{\Delta S_a^0}{R} \right) \exp\left(-\frac{\Delta H_a^0}{RT} \right) = \exp\left(\frac{\Delta S_a^0}{R} \right) \exp\left[-\frac{\Delta H_a^0}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \tag{2}$$

with T_m the average temperature of the experiments. Reparametrization leads generally to more spherical joint confidence regions of the pre-exponential factor and the activation energy and, hence, to a smaller binary correlation between the latter.

KINETIC ANALYSIS

Reaction sequence and rate equation

Table 2 represents schematically the two sequences [reactions 1–3 (**I**) and reactions 1,4–6 (**II**)] as deduced from the kinetic analysis at 303 K [13]. Actually, only sequences leading to 1-O-methyl α-D-aldehydo-glucoside had to be taken into account as the latter can be considered as a reaction intermediate and as there is no effect of the sodium 1-O-methyl α-D-glucuronate concentration on the initial reaction rates at the range of conversions investigated. The global reaction considered in Table 2 is assumed to be irreversible. This reaction sequence is in full agreement with the observations reported in the literature. The estimates of the parameters featuring in eqn. (3) are listed in Table 3. Using the parameter estimates from Table 3 it can be calculated that during oxidation an oxygen coverage of $\Theta_O = 0.8$ and a methyl α-D-glucoside coverage of $\Theta_{RCH_2OH} = 0.08$ is established at a pH of 8.

TABLE 2

Reaction sequences for the oxidative dehydrogenation of methyl α-D-glucoside to 1-*O*-methyl α-D-aldehydo-glucoside [13]

			σ_I	σ_{II}
1	$O_2 + 2*$	$\rightleftharpoons 2O*$	1	1
2	$RCH_2OH + *$	$\rightleftharpoons RCH_2OH*$	2	0
3	$RCH_2OH* + O*$	$\rightarrow RCHO + H_2O + 2*$	2	0
4	$RCH_2OH + OH^-$	$\rightleftharpoons RCH_2O^- + H_2O$	0	2
5	$RCH_2O^- + *$	$\rightleftharpoons RCH_2O^-*$	0	2
6	$RCH_2O^-* + O*$	$\rightarrow RCHO + OH^- + 2^*$	0	2
	$2\,RCH_2OH + O_2$	$\rightarrow 2\,RCHO + 2\,H_2O$		

TABLE 3

Parameter estimates with the approximate individual 95% confidence intervals obtained by regression of all data at 303 K with eqn. 3

k_3 ($kg_{cat}\,mol^{-1}\,s^{-1}$)	0.88 ± 0.32
k_6 ($kg_{cat}\,mol^{-1}\,s^{-1}$)	1.79 ± 0.23
K_1 ($m^3\,mol^{-1}$)	39.8 ± 10.0
K_2 ($10^{-3}\,m^3\,mol^{-1}$)	3.32 ± 0.61
K_5K_a/K_w ($10^{-3}\,m^6\,mol^{-2}$)	54.0 ± 12.7

$$R_W^0 = \frac{\dfrac{K_1^{1/2}}{H_{O_2}^{1/2}}p_{O_2}^{1/2}C_{RCH_2OH}L_t^2\left(k_3K_2 + k_6\dfrac{K_aK_5}{K_w}C_{OH^-}\right)}{\left(1 + \dfrac{K_1^{1/2}}{H_{O_2}^{1/2}}p_{O_2}^{1/2} + K_2C_{RCH_2OH} + \dfrac{K_aK_5}{K_w}C_{RCH_2OH}C_{OH^-}\right)^2} \tag{3}$$

Effect of the temperature on the initial reaction rate

Figs. 2 and 3 show the initial reaction rate versus the oxygen partial pressure and the methyl α-D-glucoside concentration for different temperatures in the range of 293–333 K. The maximum of the initial reaction rate versus the oxygen partial pressure shifts towards higher oxygen partial pressures with increasing temperature. It follows from eqn. (3) and the estimates for the equilibrium coefficients reported in Table 3 that, below a pH of 8.5, the oxygen partial pressure at which a maximum reaction rate occurs is approximated by:

$$p_{O_2} = \frac{H_{O_2}}{K_1}(1 + K_2C_{RCH_2OH})^2 \tag{4}$$

Eqn. (4) indicates that the oxygen partial pressure at which a maximum in the reaction rate occurs depends on both the standard adsorption enthalpies
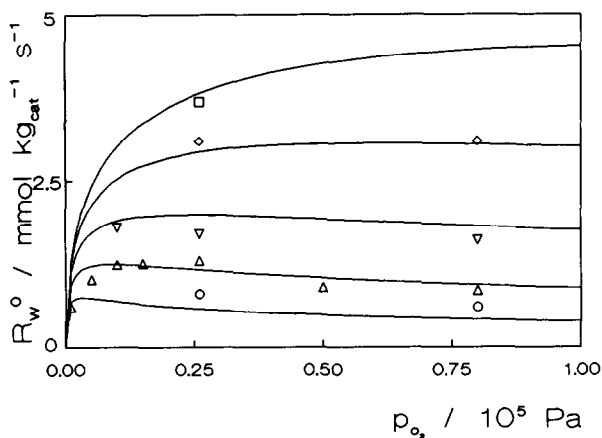
Fig. 2. Initial reaction rate versus oxygen partial pressure at various temperatures. $C_{RCH_2OH} = 100$ mol m^{-3}, pH=6, X=0.06. (O) 293 K, (△) 303 K, (▽) 313 K, (◇) 323 K, (□) 333 K. Full line: calculated with eqns. (1–3) with parameter estimates reported in Table 4.
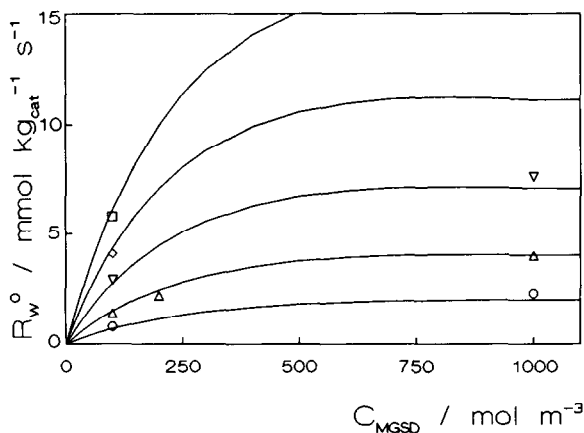
Fig. 3. Initial reaction rate versus me.-glucoside concentration at various temperatures. $p_{O_2} = 2.6 \times 10^4$ Pa, pH=9, X=0.06. (O) 293 K, (△) 303 K, (▽) 313 K, (◇) 323 K, (□) 333 K. Full line: calculated with eqns. (1–3) with parameter estimates reported in Table 4.

of oxygen and methyl α-D-glucoside. With the values presented in Table 4 it can be calculated that the partial pressure of oxygen at which a maximum rate occurs, shifts to higher values with increasing temperature, fully in agreement with Fig. 2. It also is clear from eqn. (4) that a higher partial pressure of oxygen has to be applied at a higher concentration of methylglucoside to obtain a maximum rate.

In a similar way it can be calculated that, for an oxygen partial pressure of 2.6×10^4 Pa, the methylglucoside concentration at which maximum rate occurs

TABLE 4

Estimates of apparent activation energies, pre-exponential factors, standard adsorption entropies and standard adsorption enthalpies wiht their 95% confidence intervals obtained by regression of all data with eqns. (1–3)

Reaction step from Table 2	E^a $(kJ\,mol^{-1})$	A^0 $(kg_{cat}\,mol^{-1}\,s^{-1})$
3 $RCH_2OH^* + O^* \rightarrow$	$50.5 \pm\ 6.4$	$5.5 \pm\ 0.5 \times 10^8$
6 $RCH_2O^{-*} + O^* \rightarrow$	110.5 ± 10.6	$2.7 \pm\ 0.4 \times 10^{19}$

Adsorptive	$\Delta S^0_{a,aq}$ $(J\,mol^{-1}K^{-1})$	$\Delta H^0_{a,aq}$ $(kJ\,mol^{-1})$
Oxygen	-107.4 ± 40.0	-60.0 ± 10.5
Methyl α-D-glucoside	-46.8 ± 12.8	$-17.6 \pm\ 8.3$
Methyl α-D-glucoside anion	-115.8 ± 38.7	$-61\ \pm 54$
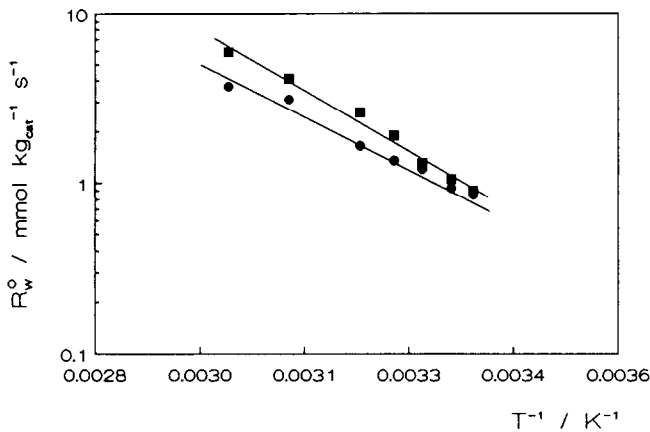
Fig. 4. Initial reaction rate versus reciprocal temperature at two pH levels. $C_{RCH_2OH} = 100$ mol m^{-3}, $p_{O2} = 2.6 \times 10^4$ Pa, $X = 0.06$. ($\bullet$): pH$=6$ ($\blacksquare$): pH$=9$. Full line: calculated with eqns. (1–3) with parameter estimates from Table 4.

shifts from 1500 to 1000 mol m^{-3} going from 293 to 333 K, which is not in contradiction with Fig. 3. These temperature effects are caused by the standard adsorption enthalpy for oxygen being more negative than that for methylglucoside, while the Henry coefficient only moderately increases with temperature.

Fig. 4 shows the reaction rate versus the reciprocal temperature. The observed linear relation indicates that the rate coefficients and Langmuir adsorption coefficients obey the Arrhenius and van 't Hoff laws. The temperature dependencies described in this section were observed at every pH investigated.

Arrhenius and Langmuir parameters

Table 4 gives the standard adsorption enthalpies, the standard adsorption entropies, the pre-exponential factors and the apparent activation energies, obtained by regression of the complete set of experimental data with eqns. (1–3). The standard adsorption enthalpies were estimated under the assumption that the ratio of the dissociation equilibrium coefficient for methyl α-D-glu-coside and the dissociation equilibrium coefficient for water, K_a/K_w, $= K_4$ does not depend on the temperature and amounts to 2×10^{-3} m^3 mol^{-1} [18].

The 95% confidence intervals within which the Arrhenius and the Langmuir parameters are estimated are rather large. Apparently the residual sum of squares is not very sensitive to the individual parameter estimates in the neigh-bourhood of the minimum. The parameter estimates are not too strongly cor-related, however. The highest binary correlation coefficient amounts to 0.96.

Figs. 2 to 4 allow a comparison of the initial reaction rates calculated ac-cording to eqns. (1–3) with the experimental data. No systematic deviations were observed. The high significance of the global regression is expressed by an F ratio of 2300.

Assessment of the activation entropies and enthalpies

The transition state theory leads to the following expression for the pre-exponential factor of a dual site reaction [19,20] for k_3 and k_6:

$$A_s^0 = \frac{eRT_m}{2N_A h} zL^{-1} \exp\left(\frac{\Delta^{\#} S^0}{R}\right) \tag{5}$$

whereby:

$$A_s^0 = \frac{A_s}{N_A} A^0 \tag{6}$$

The standard activation entropies were calculated assuming that there are six nearest neighbours of an active site and that the atom density on a platinum surface amounts to 1.4×10^{19} m^{-2} [16] resulting, for a dispersion of 0.59 and a 5% w/w Pt/C catalyst, in $A_s = 6500$ m$_{Pt}^2$ kg$_{cat}^{-1}$.

A standard activation entropy of -116 J mol^{-1} K^{-1} for the rate-determin-ing step 3, in Table 2, was calculated according to eqns. (5) and (6) and the estimates of the pre-exponential factor from Table 4. A negative standard ac-tivation entropy usually indicates a strong steric requirement for the rate-de-termining step. In this case, however, the rate-determining step is not an ele-mentary one and is preceded by an equilibrium, e.g.:

$$3\text{-}1 \ RCH_2OH^* + {}^* \quad \rightleftharpoons \ RCH_2O^* + H^*$$

$$3\text{-}2 \ RCH_2O^* + {}^* \quad \rightarrow \ RCHO + H^* + {}^*$$

$$3\text{-}3 \ H_2O + O^* + {}^* \quad \rightleftharpoons \ 2HO^*$$

$$3\text{-}4 \ HO^* + H^* \quad \rightleftharpoons \ H_2O + 2^* \ (2\times)$$

$$3 \ RCH_2OH^* + O^* \quad \rightarrow \ RCHO + H_2O + 2^*$$
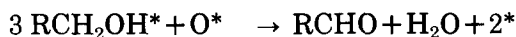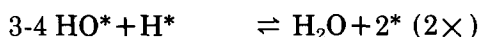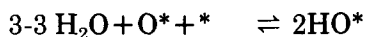
The apparent reaction rate coefficient is a product of the true reaction rate coefficient and of an equilibrium coefficient,

$$k_3^{app} = k_{3\text{-}2} K_{3\text{-}1} \tag{7}$$

hence,

$$\Delta^{\neq} S^{app} = \Delta^{\neq} S^0 + \Delta S^0 \tag{8}$$

and according to Barrow [20],

$$E^{app} = \Delta^{\neq} H^0 + RT_m + \Delta H^0 \tag{9}$$

Apparently the preceding equilibrium is accompanied by a negative change in the standard entropy. If it concerns an exothermic equilibrium it also explains the rather low activation energy.

The pre-exponential factor of the rate-determining step 6, in Table 2, is rather large and with eqns. (5) and (6) and the estimate for the pre-exponential factor from Table 4 a positive standard activation entropy of 88 J mol^{-1} K^{-1} is calculated. This rate-determining step 6 can be considered as an elementary step involving an activated complex with a more delocalized charge. This is accompanied by a decrease in solvatation which corresponds to a positive standard activation entropy [20].

A standard enthalpy of activation of 108 kJ mol^{-1} is obtained from eqn. (9) and the activation energy corresponding to step 6 in Table 4.

In summary, the Arrhenius parameter estimates corresponding to both rate-determining steps are in agreement with the transition state theory. This supports the rate equation based on the occurrence of two parallel reaction paths as presented in Table 2.

Assessment of the adsorption enthalpies

All the estimated values of the standard adsorption enthalpies for K_1, K_2 and K_5 are negative. The low absolute value of the standard adsorption enthalpy for methyl α-D-glucoside points to physisorption rather than to chemisorption which is in agreement with the hypothesis that in the reaction sequence methyl α-D-glucoside is adsorbed associatively on one site. The rate equation based on the adsorption of methyl α-D-glucoside on two sites described the data less adequately. Hence, the adsorption of methyl α-D-glucoside is believed to in-

volve only the primary hydroxyl group whereby the glucose ring is still located in the liquid.

The absolute value of the standard adsorption enthalpy for the methyl α-D-glucoside anion is larger than the standard adsorption enthalpy for methyl α-D-glucoside. This is expected because of the domination of the reaction path involving methyl α-D-glucoside anion at a pH of 10 already, which corresponds to a small concentration of the anion compared to the concentration of methyl α-D-glucoside. The strongly negative standard adsorption enthalpy of the methyl α-D-glucoside anion can be attributed to the electron deficiency of platinum caused by oxygen adsorption.

The absolute value of the standard adsorption enthalpy for oxygen is rather low compared to the -200 to -300 kJ mol^{-1}, reported for the adsorption of oxygen from the gas phase on platinum [21], although Mills et al. [22] reported values ranging from -25 to -40 kJ mol^{-1}. The combination of transmission electron microscopy and carbon monoxide-chemisorption on catalyst samples before and after oxidation did not indicate the presence of any contamination (see part III of this paper beginning on page 47 of this issue) which could be a possible explanation for low values. The difference cannot be explained by solvent effects either, which are estimated to be 12 kJ mol^{-1} [23]. It is more likely, however, that the explanation for the low value of the standard adsorption enthalpy is related to the degree of surface coverage during adsorption. The estimate for the standard adsorption enthalpy corresponds to the adsorption from the liquid phase on platinum at a surface coverage of oxygen between 0.6 and 0.8.

According to the values of the standard adsorption enthalpies and entropies reported in Table 4, the surface coverage with oxygen decreases from $\Theta_O = 0.8$ at 303 K to $\Theta_O = 0.6$ at 333 K. This is accompanied by an increase of the surface coverage with methyl α-D-glucoside from $\Theta_{RCH_2OH} = 0.08$ to $\Theta_{RCH_2OH} = 0.13$. At a pH of 10 the surface coverage with oxygen decreases from 0.6 at 293 K to 0.5 at 333 K and the surface coverage with methyl α-D-glucoside anion from 0.5 to 0.3.

Criteria for adsorption entropies

A more critical test to examine the meaningfulness of the Langmuir equilibrium coefficients is the evaluation of the standard adsorption entropy. Everett [24] has given a statistical thermodynamic derivation of the Langmuir adsorption isotherm for gases with the usual assumptions of localized adsorption on equivalent sites and a constant enthalpy of adsorption. The standard entropy change for Langmuir adsorption from the gas phase is defined as,

$$\Delta S^0_{a,g} = S^0_a - S^0_g \tag{10}$$

whereby S_g^0 is the standard entropy in the gas phase taken at unit pressure

and S_a^0 is the standard entropy in the adsorbed state at a degree of coverage of half a monolayer. Hence, the latter does not include configurational entropy but is equal to the thermal entropy of vibration and rotation. Boudart et al. [25] formulated two strict rules which must be satisfied by $\Delta S_{a,g}^0$ for non-dissociative Langmuir adsorption,

$$\Delta S_{a,g}^0 < 0 \tag{11}$$

and:

$$-\Delta S_{a,g}^0 < S_g^0 \tag{12}$$

The first rule follows from the necessary loss of entropy when a molecule is transferred without dissociation from a three-dimensional to a two-dimensional phase. The second rule expresses that a molecule can not loose more entropy than it possesses.

Boudart et al. [25] also formulated two additional relations which can be used as guidelines to assess the meaningfulness of the values obtained for $\Delta S_{a,g}^0$:

$$-\Delta S_{a,g}^0 > 42 \tag{13}$$

$$-\Delta S_{a,g}^0 \leq 51 - 0.0014 \Delta H_{a,g}^0 \tag{14}$$

Eqn. (13) is obtained by calculating the entropy loss which occurs when a gas condenses to a liquid at the critical molar volume. The equality sign in eqn. (14) corresponds to physical adsorption of a wide variety of compounds on charcoal at 273 K [24]. This guide also holds for non-dissociative chemisorption [25]. Vannice et al. [26] showed that relations (11) to (13) are also valid for dissociative adsorption.

In order to verify whether our estimates for the Langmuir parameters meet the above rules, the adsorption from the liquid phase has to be related to the adsorption from the gas phase. The standard entropy change for adsorption from the liquid phase can be defined as:

$$\Delta S_{a,aq}^0 = S_a^0 - S_{aq}^0 \tag{15}$$

Where S_{aq}^0 is the standard entropy in the liquid phase and S_a^0 the entropy in the adsorbed state at a degree of coverage of half a monolayer. Actually, S_a^0 in eqn. (15) differs from S_a^0 in eqn. 10. Eqn. 10 corresponds to a catalyst situated in the gas phase, while eqn. 15 corresponds to a catalyst in contact with an aqueous phase. In the following discussion it is assumed that the differences between those states can be neglected.

A relation between the standard entropy for adsorption from the gas phase and the standard entropy for adsorption from the liquid phase is obtained by the substitution of eqn. (15) in eqn. (10),

$$\Delta S_{a,g}^0 = \Delta S_{a,aq}^0 + S_{aq}^0 - S_g^0 \tag{16}$$

Assessment of the adsorption entropies

The standard entropy in the liquid phase, S^0_{aq}, and the standard entropy in the gas phase, S^0_g, for the three adsorptives concerned are listed in Table 5. Data concerning oxygen are well documented in the literature [23]. This is also the case for data concerning glucose in the solid state and glucose and its anion in an aqueous phase [27]. Because data on methyl α-D-glucoside are not available, the data concerning D-glucose are used. No serious deviations are expected. It is more difficult, however, to obtain useful data on related compounds and its anions in the gas phase. These data were estimated with the standard sublimation entropy and enthalpy of dimethyl D-tartrate. For the estimation of the thermodynamic data for methyl α-D-glucoside anion in the gas phase the data on the standard ionisation enthalpy and Gibbs free energy for ethanol obtained by Bohme [28] were used.

Substitution of the standard entropy from Table 5 and the standard entropy for adsorption from the liquid phase from Table 4 in relation (16), gives the standard entropy for adsorption from the gas phase. For the three adsorptives concerned the data are listed in Table 6. Table 6 also lists the standard enthalpies for adsorption from the gas phase. These standard adsorption enthalpies were obtained by substitution of the thermodynamic data from Table 5 and the standard enthalpies for adsorption from the liquid phase from Table 4

TABLE 5

Some thermodynamic properties of oxygen, glucose and glucose anion at 303 K and 1×10^5 Pa [23,27,28]

	S^0 (J mol^{-1} K^{-1})		ΔH^0 (kJ mol^{-1})
Oxygen$_g$	206	Oxygen$_{aq}$–oxygen$_g$	-11.6
Oxygen$_{aq}$	112	Glucose$_{aq}$–glucose$_s$	12.1
Glucose$_{aq}$	275	Glucose$_g$–glucose$_s$	113[a]
Glucose$_g$	476[c]	Glucose anion$_{aq}$–glucose$_{aq}$	-8[b]
Glucose anion$_{aq}$	270[b]	Glucose anion$_g$–glucose$_g$	-84[d]
Glucose anion$_g$	384[e]		

[a]Assumed to be equal to the standard sublimation enthalpy for dimethyl D-tartrate.
[b]In alkaline media.
[c]Estimated with the standard sublimation entropy of dimethyl D-tartrate.[d]
[d]Average standard reaction enthalpy at 298 K for: $OH^- + ROH \rightleftharpoons RO^- + H_2O$, where ROH stands for a small primary alcohol such as CH_3CH_2OH.
[e]Calculated with $\Delta H^0_{ion,g}$ [d] and $\Delta G^0_{ion,g}$ for the reaction: $OH^- + CH_3CH_2OH \rightleftharpoons CH_3CH_2OH^- + H_2O$ at 298 K.

TABLE 6

Standard entropies and standard enthalpies for adsorption from the gas phase at 303 K, calculated by substitution of the standard adsorption entropies and enthalpies from Table 4 and the thermodynamic data from Table 5 in eqns. (16) and (17)

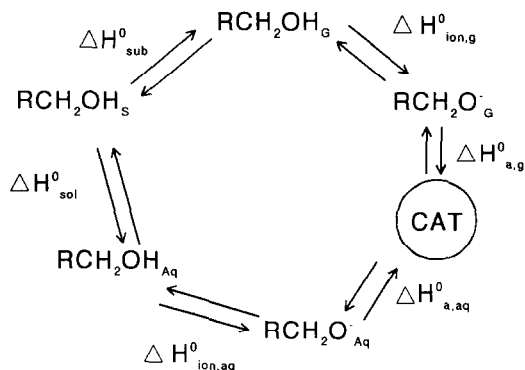| Adsorptive	$\Delta S^0_{a,g}$ (J mol^{-1} K^{-1})	$\Delta H^0_{a,g}$ (kJ mol^{-1})
Oxygen	-201	-72
Methyl α-D-glucoside	-248	-120
Methyl α-D-glucoside anion	-230	-86

Fig. 5. Born–Haber cycle for the determination of $\Delta H^0_{a,g}$.

in a relation analogous to relation (16). The relation between the enthalpy for adsorption from the gas phase and the enthalpy for adsorption from the liquid phase for the methyl α-D-glucoside anion, as an example, is given by:

$$\Delta H^0_{a,g} = \Delta H^0_{a,aq} + \Delta H^0_{sol} + \Delta H^0_{ion,aq} - \Delta H^0_{sub} - \Delta H^0_{ion,g} \tag{17}$$

as follows from the cycle shown in Fig. 5.

All standard entropies for adsorption from the gas phase, listed in Table 6, fulfil the rules (11) to (13), but not guideline (14).

The fact that the standard entropies for adsorption from the gas phase for all three adsorptives do not meet guideline (14) is probably due to deviation from ideal solutions behaviour and to the rather rough estimates for the standard sublimation and ionisation enthalpies and entropies, assumed in the above calculations.

Hence, from the above evaluation of the standard adsorption entropies it follows that the Langmuir equilibrium coefficients appearing in eqn. (3) are meaningful. This indicates that the use of a Langmuir isotherm to describe the kinetics over the investigated range of conditions was justified. The physically

meaningful Langmuir equilibrium coefficient for oxygen in particular supports the hypothesis of reversible rather than irreversible adsorption of oxygen.

CONCLUSIONS

The initial kinetics of the selective oxidation of methyl α-D-glucoside on supported platinum can be described adequately over a broad range of reaction conditions by a relatively simple rate equation of the Langmuir-Hinshelwood type, based on two reaction paths: one involving adsorbed methyl α-D-glucoside and dominating at low pH, the other involving the adsorbed methyl α-D-glucoside anion and dominating at high pH. Both reaction paths contain a rate-determining step consisting of a surface reaction between these species and chemisorbed oxygen. The assessment of the Arrhenius parameter estimates within the framework of the transition state theory showed that these rate-determining steps lead to physically meaningful estimates. The rate equation contains Langmuir adsorption terms accounting for the competitive reversible dissociative chemisorption of oxygen and for the reversible associative adsorption of methyl α-D-glucoside and methyl α-D-glucoside anion. The Langmuir adsorption isotherms are physically meaningful as was shown by the examination of the estimates for the corresponding standard adsorption entropies and enthalpies.

NOTATION

A^0	Preexponential factor of the reaction rate coefficient, $\mathrm{kg_{cat}\ mol^{-1}}$ $\mathrm{s^{-1}}$ or $\mathrm{m^2\ s^{-1}}$
A_s	Catalyst surface area, $\mathrm{m^2_{Pt}\ kg^{-1}_{cat}}$
C	Concentration, $\mathrm{mol\ m^{-3}}$
e	Euler number
E^a	Apparent activation energy, $\mathrm{J\ mol^{-1}}$
H	Henry coefficient, $\mathrm{Pa\ m^3\ mol^{-1}}$
H^0	Standard enthalpy, $\mathrm{J\ mol^{-1}}$
h	Planck constant, $\mathrm{J\ s}$
k	Reaction rate coefficient, $\mathrm{kg_{cat}\ mol^{-1}\ s^{-1}}$
K	Equilibrium adsorption coefficient, equilibrium rate coefficient, or, $\mathrm{m^3\ mol^{-1}}$
K_a	Equilibrium dissociation coefficient of methyl-α-D-glucoside, $\mathrm{m^3}$ $\mathrm{mol^{-1}}$
K_w	Equilibrium dissociation coefficient of water, $\mathrm{m^6\ mol^{-2}}$

L Site number density, m_{Pt}^{-2}
L_t Surface concentration of active sites, mol kg_{cat}^{-1}
N_A Avogadro constant, mol^{-1}
p Partial pressure, Pa
R Gas coefficient, J mol^{-1} K^{-1}
R_W Production rate, mol kg_{cat}^{-1} s^{-1}
S^0 Standard entropy, J mol^{-1} K^{-1}
T Temperature, K
T_m Average temperature of all experiments, K
X Conversion
z Number of nearest neighbors

Greek symbols

θ Degree of surface coverage
σ Stoichiometric number

Subscripts

a   Adsorption
aq   Aqueous phase
g   Gas phase
ion   Ionization
RCH_2OH Methyl α-D-glucoside
s   Surface
sol   Solubility
sub   Sublimation

Superscript

0   at time = 0 s, standard
'   Reparametrized
Activation
*   Active site

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