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Aerobic oxidation of glucose I. Enzymatic catalysis

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Abstract

The selective oxidation of D-glucose to D-gluconic acid was performed at atmospheric pressure, controlled pH value, and constant oxygen concentration, in the temperature range from 273.2 to 303.2 K, using Hyderase (a commercial glucose oxidase and catalase preparation). Measurements of initial rate as a function of initial glucose concentration were interpreted by a simplified version of the already proposed reaction mechanism, having the form of a simple equation of the Michaelis–Menten type, with two kinetic parameters, i.e., k_1 referring to the reaction between glucose and oxidized enzyme, and k_c referring to a combination of the other steps. The activation energy for k_1 was found to be 49.6 kJ mol^{-1}; an apparent activation energy of 26.7 kJ mol^{-1} was obtained for k_c.

Keywords: Glucose oxidase; Kinetics; Activation energy; Michaelis–Menten equation

1. Introduction

Enzymatic catalysis and chemical catalysis are the basis of many industrial processes and often these different technologies compete for the synthesis of important chemicals. Thus, lactic acid, propane-1,3-diol, and many pharmaceutical intermediates can be synthesized by using either chemical or biochemical processes where catalytic steps are of great relevance.

In many cases, however, only one industrial route is known owing to economical reasons and, in particular, no chemical processes are known for the production of gluconic acid and gluconates.

In fact, D-gluconic acid and its δ-lactone are simple dehydrogenation products of D-glucose obtained by different microorganisms as discovered by Boutroux [1]. Molliard first detected gluconic acid in cultures of *Aspergillus niger* which convert glucose to this product in high yields especially upon acid neutralization with calcium carbonate [2–4]. Later, Currie et al. obtained the first modern patent covering the production of gluconic acid by *Penicillium* or *Aspergillus* employing the modern technique of submerged culture of molds with stirring and aeration of the fermentation medium [5]. Yields as high as 90% in 48 to 80 h were claimed for both *Penicillium* and *Aspergillus*. Finally a strain of *A. niger* (Strain 67) was obtained by selection [6]. With this last fungi yields of up to 95% from 150 to 200 g L^{-1} solutions in 24 h were obtained in a pilot plant. Elevated air pressure (from 2 to 4 bar) and neutralization with calcium carbonate were later applied. In 1952 a process for the production of sodium gluconate, where the acid produced was neutralized by NaOH to pH 6.5, was developed [7]. This process forms the basis of modern plant operations in deep-tank fermentation.

Further developments for prolonging catalytic stability and productivity led to the proposal of immobilized enzyme or fungi on different support matrices [8,9]. Moreover, in the last decade a new growing interest on different aspects of the enzymatic oxidation using glucose oxidase or its modifications has been observed [10–15].

Although the simple aerobic oxidation represents the most investigated technology, other oxygen-containing molecules have been used either to increase the local concentra-

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tion of O_2, by adding H_2O_2 into the reaction medium [16], or to gain insight into the reaction mechanism, as in the case of quinones [17].

Owing to the complexity of the fermentation process, interest exists for an alternative environmental friendly technology based on the use of air, or molecular oxygen, in water solution with the aid of heterogeneous catalysis.

The chemical oxidation of glucose to gluconic acid with Pd group metals has been investigated for a long time [18]. Working under mild conditions (303–323 K, 101 kPa), the reaction can be carried out with high conversion and good selectivity but the catalyst deactivates by self-poisoning and overoxidation. In more recent studies sophisticated bi- and trimetallic catalysts have been proposed to overcome these effects. In particular, Bi-promoted catalysts showed the best performance [19,20]. However, to our knowledge, no industrial application of platinum metal catalysts has been currently applied.

In recent years it has been found that Au-catalyzed liquid-phase oxidation of alcohols and aldehydes to the corresponding acid could be an alternative route to Pd group metals [21–23]. In particular, naked and supported metal nanoparticles (average diameter 3–5 nm) resulted in extremely efficient oxidation of glucose allowing a reaction rate comparable to that of enzymatic systems [24].

These results prompted us to carry out a deeper investigation on enzymatic and inorganic catalysis and for this reason we have undertaken a comparative study of their reaction kinetics under similar experimental conditions.

This paper deals with the results of the homogeneous glucose oxidation catalyzed by Hyderase, a commercial system containing glucose oxidase and catalase as active components. A second study, concerning the kinetic behavior of colloidal gold sols under quasihomogeneous conditions, will follow along with a comparison with recent kinetic investigations on heterogeneous gold catalyst [25].

2. Experimental

2.1. Reagents and apparatus

D-Glucose monohydrate (99% pure) and δ-gluconolactone (99% pure) from Fluka were used as reagent and reference compound without further purification. NaOH (Merck) was 99.9% pure and stored under nitrogen. Gaseous oxygen and nitrogen (SIAD) were 99.99% pure. MilliQ water obtained by an Academic A-10 Millipore apparatus was used as solvent for all experiments.

2.2. Enzymatic system

The enzymatic catalyst was a commercial glucose oxidase and catalase preparation (Hyderase) produced by *A. niger* fermentation (Amano Enzyme Co., UK), which was claimed to contain 1 mg g^{-1} of FAD (flavine-adenine dinucleotide) and not less than 15,000 units g^{-1}. (Unit definition: required amount of enzyme to oxidize 1 µmol of glucose to gluconic acid and H_2O_2, per minute at 25 °C and pH 7.) The absence of free apoenzyme in this preparation was proved by observing no benefit upon FAD addition.

2.3. Procedure for kinetic studies

2.3.1. Oxidation of glucose

All the experiments were carried out in a semibatch reactor (50 mL) at controlled temperature (±0.1 K), pH value (±0.1), and magnetic stirring (1700 rpm), by using a 751 GPD Titrino (Metrohm) equipped with NaOH as titration reagent. Oxygen and nitrogen (total flow 100 N cm^3 min^{-1}) were mixed in different ratios using mass-flow instruments (Brooks 5850E controlled by a Brooks 5878 gas controller) and bubbled at atmospheric pressure through the aqueous solution of glucose at different concentrations (0.100, 0.050, 0.033, and 0.025 M). For these concentration values, substrate inhibition effects were not found [14]. A Hyderase concentration of 0.0118 g L^{-1} (corresponding to 1.5×10^{-8} mol L^{-1} of FAD) was used in all experiments. The activation energy was evaluated in the temperature range from 273.2 to 303.2 K ($\Delta T = 10$ K). Glucose oxidation was started by adding the enzyme to the gas-saturated solution of glucose under stirring, while NaOH was automatically added to neutralize the reaction product, gluconic acid, at pH 7.

2.3.2. Evaluation of reaction rate

Gluconic acid concentration vs time plots were derived from the NaOH addition rate. After an initial induction period (200–300 s) the plots of $\Delta C_{\text{Gluconic}}$ vs time were linear ($R \geqslant 0.998$) up to 5–10% fractional conversion (Fig. 1), thus allowing the use of the initial rate method. This method avoids problems of product inhibition [14]. The zero time was taken after 500 s from the enzyme addition.

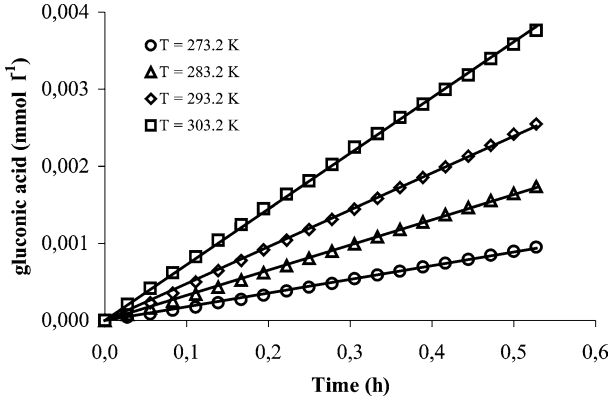


Fig. 1. Examples of initial rate determination for the glucose oxidation under pH controlled conditions for different temperature values. Reaction conditions: glucose 0.100 mol L^{-1}; [Hy] 0.0118 g L^{-1}; total flow of O_2–N_2 mixture 100 N cm^3 min^{-1}; stirring rate 1700 rpm. The pH was maintained at 7 by automatic NaOH addition.

Table 1
Parameters [26] used to calculate solubility of oxygen and nitrogen in water by the following equation where X_i is expressed in mol O_2/mol H_2O and T in Kelvin

Gas	A	B	C	Temperature range (K)	SD
O_2	−66.7354	87.4755	24.4526	273.15–348.15	±0.36%
N_2	−67.3877	86.3213	24.7981	273.15–348.15	±0.72%

$\ln(X_i) = A + B/T^* + C \ln T^*$, where $T^* = T/100$.

2.3.3. Oxygen–nitrogen ratio

The solubility of oxygen in the reacting solution was mainly dependent on temperature and less on glucose concentration (from 0.100 to 0.025 M). Therefore, different oxygen molar fractions in the gas phase, calculated according to the reported smoothing equation and related table (Table 1) [26], have been used at different temperatures. A constant concentration of dissolved oxygen ($1.18 \pm 0.15 \times 10^{-3}$ M) was measured with an AMEL instrument equipped with an AMEL 332/P electrode throughout the experiments.

2.3.4. Diffusional effects

In order to avoid gas-mass-transfer control during glucose oxidation, stirring rate, oxygen flow, and enzyme concentration were optimized at the highest temperature investigated (303.2 K) and using a 0.100 M glucose solution. Over 1400 rpm, no rate control by oxygen was found using more than 50 N cm^3 min^{-1} of O_2 and enzyme concentration below 0.118 g L^{-1}. Therefore, the standard kinetic experiments were carried out at 1700 rpm, with a total gas flow of 100 N cm^3 min^{-1}, and using an Hyderase concentration of 0.0118 g L^{-1}.

2.4. Effect of the oxygen concentration on the reaction rate

Another set of kinetic measurements was carried out under the same conditions and at the same temperatures as the standard runs, but using a constant glucose concentration (0.100 M) and different O_2 molar fractions. In these experiments the oxygen concentrations investigated were 1.18×10^{-3}, 8.85×10^{-4}, 5.90×10^{-4}, and 2.48×10^{-4} M. This last value was obtained using air.

2.5. Evaluation of the H_2O_2 production

Owing to the known inhibition of hydrogen peroxide on glucose oxidase [27–31], quantitative determinations of this by-product have been done during the runs: no free hydrogen peroxide was detected throughout the experiments.

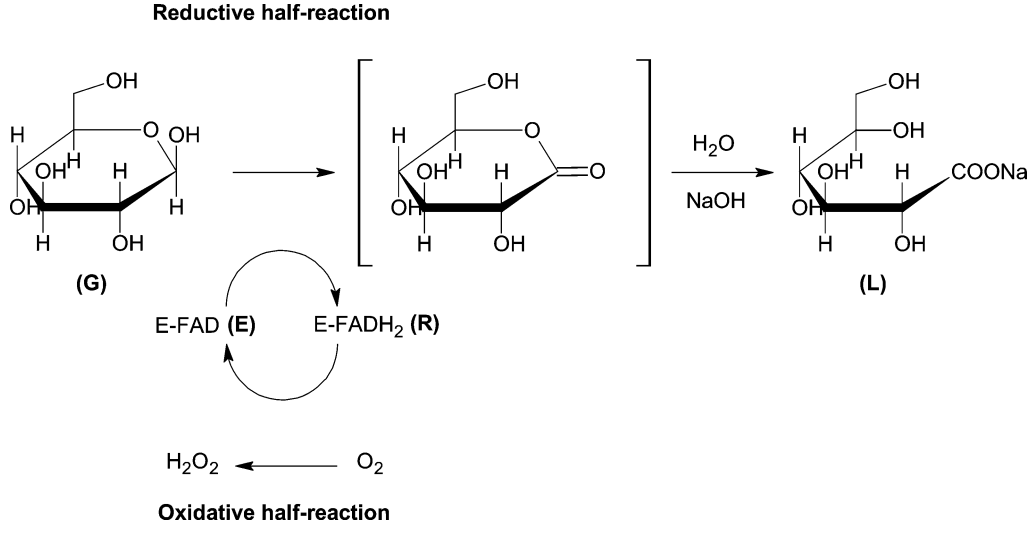
2.6. Analysis of product

The only product of glucose oxidation was identified as gluconic acid by comparison with the standard compound. The analysis was performed by HPLC on a Varian 9010 instrument equipped with a Varian 9050 UV (210 nm) detector. An Alltech OA-1000 column (300 × 6.5 mm) was used with aqueous H_2SO_4 0.01 M (pH 2.1) (0.4 mL min^{-1}) as the eluent.

3. Results and discussion

Glucose oxidase from *A. niger* is the key factor for the enzymatic glucose oxidation. It is a flavoprotein, a homodimer of molecular weight 150 to 180 kDa, containing two tightly bound flavin adenine dinucleotide molecules [32]. Dissociation of the subunits is possible only under denaturating conditions and is accompanied by the loss of the FAD cofactor.

According to the accepted Scheme 1 [33], the conversion of glucose to gluconic acid or gluconate can be represented by rather simple reactions where δ-lactone formation is catalyzed by glucose oxidase (EC 1.1.3.4). This reaction involves the direct consumption of 1 mol of oxygen per mole



Scheme 1.

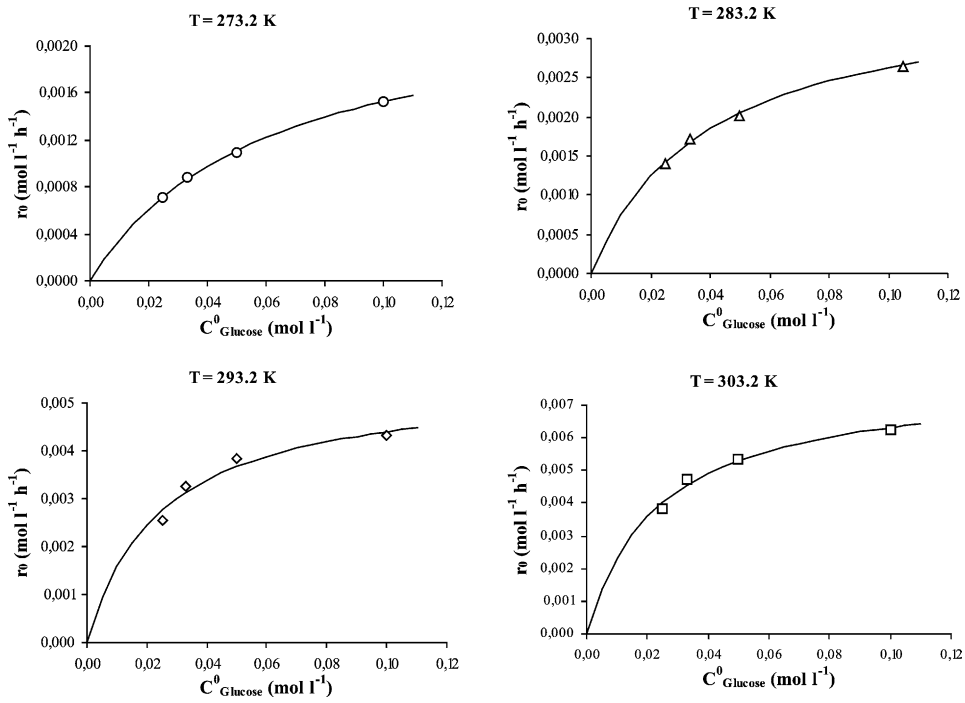


Fig. 2. Plots of initial rate vs initial glucose concentration for the runs under standard conditions at the different temperatures. The curves were calculated by Eq. (10), using the parameter values of Table 3.

of glucose resulting in the formation of hydrogen peroxide; this by-product is cleaved by catalase (EC 1.11.1.6). The glucono-lactone is converted to gluconate by spontaneous hydrolysis.

The mechanism of the glucose oxidase reaction has been extensively studied and a detailed reaction scheme has been proposed [34–39]. According to this model, the reaction can be divided into two main half-reactions, the oxidation of substrate with the corresponding reduction of the enzyme in the reductive half-reaction, and the subsequent reoxidation of the enzyme in the oxidative half-reaction.

Nakamura and Ogura [40], and in more detail Gibson et al. [34], derived a mechanism involving four steps according to

$$E + G \xrightarrow{k_1} RL, \tag{1}$$

$$RL \xrightarrow{k_2} R + L, \tag{2}$$

$$R + \mathrm{O_2} \xrightarrow{k_3} E \cdot \mathrm{H_2O_2}, \tag{3}$$

$$E \cdot \mathrm{H_2O_2} \xrightarrow{k_4} E + \mathrm{H_2O_2}, \tag{4}$$

where E is the oxidized enzyme, R is the reduced enzyme, G is the D-glucose, and L is the gluconate, while RL and $E \cdot \mathrm{H_2O_2}$ are complexes between enzyme and products. Gibson and Bright [35] and Duke et al. [37], using deuterated glucose and an oxygen electrode, were able to demonstrate that two additional reactions could be taken into account

$$E + G \longleftrightarrow EG, \tag{5}$$

$$RL + G \longrightarrow R + L + G. \tag{6}$$

Recently, other studies were performed on glucose oxidation and new results were obtained on the determination of the rate parameters at 298.2 K [10] and 303.2 K [14].

However, despite many detailed investigations, no experimental values of the activation energies controlling the main oxidation steps were, to our knowledge, reported.

In the present study, experiments devoted to this latter scope were performed at the fixed pH value of 7 by using an automated apparatus that allowed the titration, in real time, of the gluconic acid produced. Examples are given in Fig. 1. Several runs were carried out for each C^0_{Glucose} and temperature value. Initial rates (r_0) were obtained averaging the slopes of the plots corresponding to a given condition. With this procedure the experimental r_0 values reported in Fig. 2 have been derived.

A stationary-state treatment, taking into account the most significant steps of the process, i.e., steps (1)–(4), gives [37]

$$\frac{C^0_{\mathrm{E}}}{r} = \frac{1}{k_2} + \frac{1}{k_4} + \frac{1}{k_3 \cdot C_{\mathrm{O_2}}} + \frac{1}{k_1 \cdot C_{\mathrm{Glucose}}}. \tag{7}$$

Standard kinetic runs were carried out at constant oxygen concentration ($C_{\mathrm{O_2}} = 0.00118\ \mathrm{mol\,L^{-1}}$, corresponding to an aqueous solution saturated by oxygen at 303.2 K), with $C^0_{\mathrm{E}} = 0.0118\ \mathrm{g\,L^{-1}}$, so that a composite coefficient k_{c} can be defined as in

$$\frac{1}{k_{\mathrm{c}}} = \frac{1}{k_2} + \frac{1}{k_4} + \frac{1}{k_3 \cdot C_{\mathrm{O_2}}} \tag{8}$$

Table 2
Initial reaction rate under different glucose concentrations and for the temperature values investigated for $C_{O_2} = 1.18 \times 10^{-3}$ mol L^{-1} and $C^0_{\text{Hyderase}} = 0.0118$ g L^{-1}

T (K)	[$C_6H_{12}O_6$] (mol L^{-1})	r_0 (mol L^{-1} h^{-1})
273.2	0.100	0.001528
	0.050	0.001095
	0.033	0.000879
	0.025	0.000710
283.2	0.100	0.002641
	0.050	0.002019
	0.033	0.001715
	0.025	0.001411
293.2	0.100	0.004309
	0.050	0.003826
	0.033	0.003254
	0.025	0.002564
303.2	0.100	0.006250
	0.050	0.005362
	0.033	0.004748
	0.025	0.003812

and, for initial rate measurements, Eq. (7) assumes the Lineweaver–Burke form of Eq. (9),

$$\frac{1}{r_0} = \frac{1}{k_c \cdot C^0_E} + \frac{1}{k_1 \cdot C^0_E} \cdot \frac{1}{C^0_{\text{Glucose}}}, \tag{9}$$

or the equivalent Michaelis–Menten form of Eq. (10):

$$r_0 = \frac{k_c \cdot C^0_E \cdot C^0_{\text{Glucose}}}{k_c/k_1 + C^0_{\text{Glucose}}}. \tag{10}$$

The measured r_0 values are presented in Table 2.

A first evaluation of the parameters k_1 and k_c was obtained by Eq. (9), followed by a refinement obtained by a nonlinear regression routine [41], applied to Eq. (10), with an objective function, to be minimized, defined as $F = \Sigma(r_{0,\text{exptl}} - r_{0,\text{calcd}})^2/2$. The final values are collected in Table 3. The curves of r_0 vs C^0_{Glucose}, calculated by these values, are compared with the experimental points in Fig. 2: the agreement is generally good, although slightly less satisfactory for the runs at 293.2 K.

The influence of oxygen concentration on r_0 has experimentally been checked in order to assign the relative weight to the term $1/(k_3 C_{O_2})$. Working at different oxygen concentrations (1.18×10^{-3}, 8.85×10^{-4}, 5.90×10^{-4}, and 2.48×10^{-4} M), and keeping a constant glucose and enzyme concentration (0.100 mol L^{-1} and 0.0118 g L^{-1}, respectively), tests have been performed at 273.2, 283.2, 293.2, and 303.2 K. The plots of $1/r_0$ vs $1/C_{O_2}$ gave roughly straight lines; their slope, interpreted as $1/(k_3 C^0_E)$, as from Eq. (7), allowed evaluation of only the order of magnitude of k_3. This was due to experimental uncertainty and to the scarce dependence of k_3 on temperature [34]. The results indicate that the values of $1/(k_3 C_{O_2})$ during the standard runs are a small fraction of $1/k_c$, at most 15%. Therefore the term $1/k_c$ is mainly a combination of $1/k_2$ and $1/k_4$. Since literature values [34,37] indicate that k_2 is larger than k_4 already at 273.2 K and even more at higher temperatures, the term $1/k_4$ should have a prevailing weight: in other words, k_c appears to be a rough approximation of k_4 or better a lower limit for such coefficient, which corresponds to the dissociation rate of adduct $E \cdot H_2O_2$.

Table 3
Evaluation of k_c and k_1 for the temperatures investigated

T (K)	k_c (mol g^{-1} h^{-1})	k_1 (L g^{-1} h^{-1})
273.2	0.2076	3.425
283.2	0.3108	7.908
293.2	0.4652	18.79
303.2	0.6606	28.10

At the optimum, the objective function F had values $\leqslant 4 \times 10^{-8}$; the standard error of the estimate of the variables ($\sigma = F^{1/2}$) is therefore $\leqslant 0.0002$ for r_0.

A comparison with values previously published for the different coefficients, using molar concentrations for the enzyme, is possible by considering that our catalyst is given as containing 1 $\text{mg}_{\text{FAD}}\,\text{g}^{-1}_{\text{Hyderase}}$, that is 1.3×10^{-6} $\text{mol}_{\text{FAD}}\,\text{g}^{-1}$. Therefore the order of magnitude of coefficient k_3 (of the order of 5×10^3 L g^{-1} h^{-1}) is convertible into 1×10^6 L mol^{-1} s^{-1}. The values given previously (from 1.3×10^6 to 2.4×10^6 L mol^{-1} s^{-1} in the range 273.2–303.2 K) [34,37] were of the same order of magnitude. The value of the composite coefficient k_c in Table 3 for $T = 273.2$ K can be converted into $k_c = 45$ s^{-1}; the published k_4 values are 360–370 s^{-1} [34,37]; for $T = 303.2$ K, we found $k_c = 145$ s^{-1}; the published k_4 value is ca. 1350 s^{-1} [37]. Due to the approximations made, it seems an acceptable disagreement.

As to the coefficient k_1, the value in Table 3 for $T = 273.2$ K can be converted into $k_1 = 750$ L mol^{-1} s^{-1}; the value for $T = 303.2$ K is equivalent to 6100 L mol^{-1} s^{-1}. Higher values are found in the literature: at 273.2 K, $k_1 = 2100$ L mol^{-1} s^{-1} was given by Gibson et al. [34] and $k_1 \cong 3600$ L mol^{-1} s^{-1} was given by Duke et al. [37]; at 303.2 K, $k_1 \cong 21{,}000$ L mol^{-1} s^{-1} was given by Duke et al. [37]. However, the disagreement is within one order of magnitude, and could be due to the approximately reported concentration of enzymatic catalyst [37].

A further comparison with recent work, based on a simple Michaelis–Menten model, can also be made. Using the following rate equation $r = k_{\text{cat}} C^0_E C_S/(K_M + C_S)$, for runs at 298.2 K, values of $k_{\text{cat}} = 508$ s^{-1} and $K_M = 0.028$ mol L^{-1} were reported [10] to be compared with our results, interpolated by the Arrhenius equation, $k_c = 121$ s^{-1} and $k_c/k_1 = 0.024$ mol L^{-1}, respectively. Using the following rate equation: $r = V_m C_S/(K_M + C_S)$, for runs at 303.2 K, values $V_m = 8.05$ mmol L^{-1} min^{-1} and $K_M = 2.61$ g L^{-1} were reported [14] to be compared with our values $k_c C^0_E = 0.130$ mmol L^{-1} min^{-1} and $k_c/k_1 = 4.32$ g L^{-1}, respectively. While a good or fair agreement can be observed in the case of K_M and our related k_c/k_1 values [10,14] and an acceptable disagreement is noted in the case of k_{cat} and k_c [10], the rate parameter $k_c C^0_E$ is quite far from V_m [14].

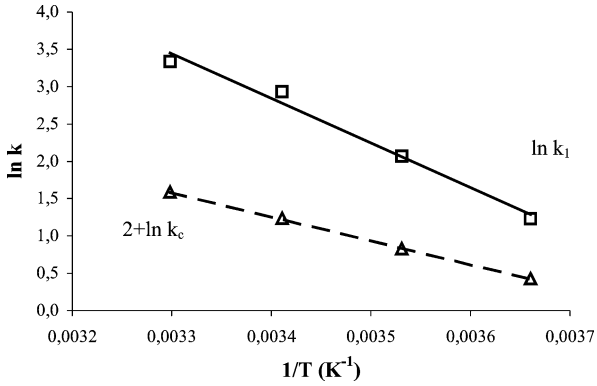


Fig. 3. Arrhenius plots for the k_c and k_1 coefficients.

However, in this latter case, V_m includes an enzyme concentration which is not precisely reported, but probably much higher than in our experiments.

The coefficient k_1 was represented as a function of temperature by the Arrhenius equation (Fig. 3), obtaining $\ln A_1 = 23.1 \pm 1.8$ (A_1 in L g^{-1} h^{-1}) and an activation energy $E_{a_1} = 49.6 \pm 4.4$ kJ mol^{-1}. The analogous plot for k_c (Fig. 3) gave $\ln A_c = 10.2 \pm 0.1$ (A_c in mol g^{-1} h^{-1}) and an apparent activation energy $E_{a_c} = 26.7 \pm 0.3$ kJ mol^{-1}.

It is noteworthy that the values of k_c and of $k_1\ C^0_{\text{Glucose}}$ are of the same order of magnitude under our experimental conditions, in particular at the lower temperatures (273.2 and 283.2 K); at higher temperatures, $k_1\ C^0_{\text{Glucose}}$ becomes larger than k_c, because E_{a_1} is considerably larger than E_{a_c}. The difference between the values of E_{a_1} and E_{a_c} seems reasonable, because the former represents the activation energy of a redox step, while the latter approximately reflects the activation energy of the dissociation of an enzyme-product adduct.

4. Conclusions

The rate of glucose oxidation as a function of substrate concentration fits the simplified version of the reaction mechanism, having the form of a Michaelis–Menten equation with two kinetic parameters. This is useful in view of a comparison with the inorganic catalysis, where a Langmuir–Hinshelwood model has recently been proposed [25].

The accurate determination of the kinetic parameters allowed calculation, for the first time, of the activation energy for the step concerning the reaction of glucose with the oxidated form of the enzyme to give the complex between the product and the reduced enzyme (k_1). The apparent activation energy was also determined for the composite coefficient k_c embodying all other steps.

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