Hydrolysis of methyl α- and β-D-glucopyranosides in the presence of a dealuminated H-Y faujasite

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Hydrolysis of methyl α- and β-D-glucopyranosides was performed in the presence of protonic-form zeolites such as a dealuminated Y-faujasite with a Si/Al ratio of 15, at temperatures ranging between 100 and 150 °C, and in water as the solvent. The β/α ratio for the hydrolysis reaction rates was found to be equal to 5–6, whereas a ratio of 2–3 was reported in the literature for the homogeneous reaction. The observed higher β/α ratio is proposed to result from the reinforcement of stereoelectronic effects which were shown to apply in reactions taking place on the surface of a solid. Those effects operate in a classical manner on a molecular standpoint, but they are reinforced due to the favorable interaction of oxygen electron lone pairs with the electron-deficient species present on the surface of the solid, protonic species in the case of zeolites.

Keywords: hydrolysis, alkyl glycosides, zeolites, stereoelectronic effects

1. Introduction

In recent papers, we have reported on the possibility for stereoelectronic effects to occur in heterogeneous acid-catalyzed hydrolysis of acetals, O,S-acetals and thioacetals [1] as well as in hydrolysis of disaccharides such as maltose and cellobiose [2]. Those effects were proposed to result from a more favorable adsorption due to the proper orientation of oxygen or sulfur electron lone pairs, thus leading to a better electron transfer to protonic species present on the surface of the solid. As a consequence, the classical stereoelectronic effects involved on a molecular standpoint were found to be reinforced in the presence of solid catalysts.

Another reaction of interest is the hydrolysis of alkyl α- and β-D-glucopyranosides since the lower reactivity of the alkyl α-D-glucopyranosides was initially attributed to the reverse anomeric effect [3], whereas, from a recent study on model compounds of α- and β-D-glycosides [4], these results were explained in terms of stereoelectronic effects by the differences in energy between ground-state and transition-state conformation [5]. Rigid models of α-glycosides were shown to hydrolyze through their ground-state conformation, whereas β-glycosides must assume a boat conformation to fulfill the stereoelectronic requirement of the antiperiplanar electron lone pair orientation as shown in scheme 1.

It was then interesting to investigate further the hydrolysis of methyl α- and β-D-glucopyranosides in the presence of solid catalysts such as acidic zeolites. Apart from their acidic properties, those materials are known, on one hand, for their shape-selectivity properties, i.e., the accessibility to the catalytic sites might be modified as a function of both internal diameter of the catalyst and kinetic diameter of the reactants. They are also known, on the other hand, for their adsorbent properties, i.e., reactants might be adsorbed in a different manner depending on their conformation in both ground and transition state.

2. Experimental

Hydrolysis reactions were carried out in a magnetically stirred 0.1 l batch reactor (Autoclave Engineers Magne-Drive) working in the batch mode, at temperatures ranging from 100 to 150 °C and 800 rpm of agitation speed. The feed consisted of a 0.15 M solution of alkyl-D-glycoside in water in the presence of 1 g of freshly calcined catalyst (CBV 720 from PQ Zeolites, calcination in flowing air at 500 °C).

The course of the reaction was followed by HPLC using a Shimadzu LC-6A pump and a refractive index RID-6A detector. Hydrolysis of methyl α-D-glucopyranoside was followed by using a SARASEP Car-H column thermostated at 70 °C, with sulfuric acid 10^{-3} M as eluent and citric acid as external standard. Hydrolysis of methyl β-D-glucopyranoside was followed by using a SHANDON $-NH_2$ column with acetonitrile/water (70/30 v/v) as eluent and saccharose as external standard. Initial hydrolysis reaction rates were deduced in a classical manner from the plots of concentrations in reactants and products as a function of time.

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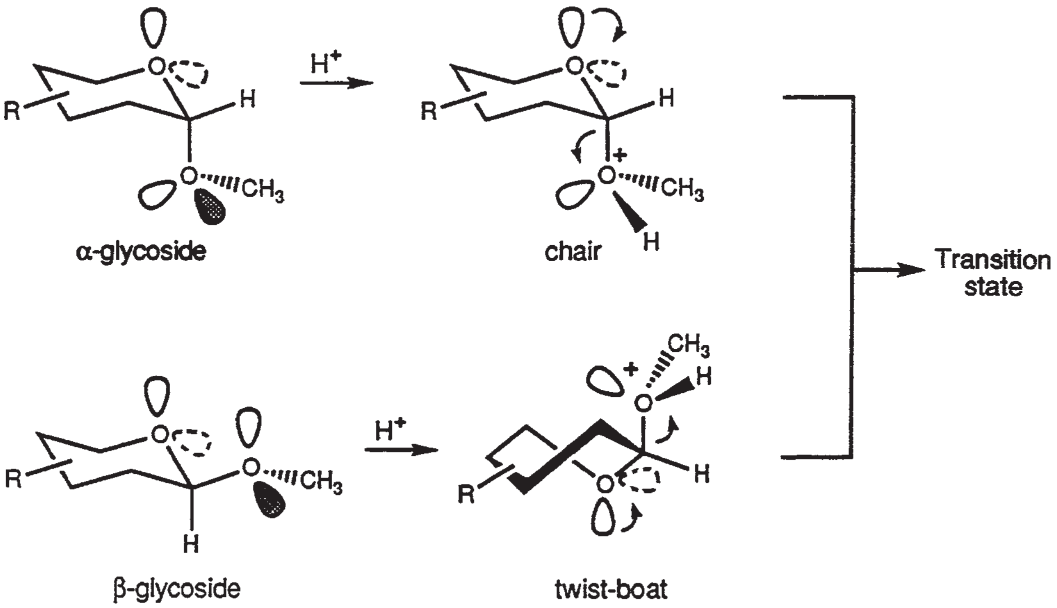

Scheme 1. Stereoelectronic effects in hydrolysis of methyl D-glucopyranosides.

3. Results

Under those experimental conditions, it was important to show that acid hydrolysis of alkyl α- and β-D-glucopyranosides was working under chemical regime and was not controlled by external or internal diffusional limitations. The importance of external diffusion can be estimated from several parameters:

(i) Plots of initial reaction rates as a function of agitation speed show that no mass-transfer limitation occurs at agitation speed over 400 rpm (figure 1);

(ii) Arrhenius plot for hydrolysis of methyl α-D-glucopyranoside (figure 2) shows that the calculated energy of activation (124 kJ/mol) is largely over the limit value of 40 kJ/mol for a reaction controlled by mass-transfer limitation. Furthermore, the activation energy measured is of the same order of magnitude as for the homogeneous hydrolysis reaction, 130–140 kJ/mol [3], illustrating once again, that the mechanistic concepts developed in homogeneous catalyzed reactions can also apply to reactions catalyzed by solids [6];

(iii) Plots of initial reaction rates for hydrolysis of methyl α-D-glucopyranoside as a function of catalyst weight and initial concentration in reactant are reported in figures 3 and 4, respectively. From both figures it can be seen that the reaction obeys a classical Langmuir–Hinshelwood mechanism in which products and solvent are not involved in the rate equation, $r_0 = k\lambda_{\text{glycoside}}[\text{glycoside}]/(1+\lambda_{\text{glycoside}}[\text{glycoside}])$, where k is the reaction rate constant, $\lambda_{\text{glycoside}}$ the coefficient of adsorption of the glycoside, and [glycoside] the concentration in glycoside. As shown in the plot of the initial reaction rates against the catalyst weight (figure 3), at low coverage of the catalyst, an apparent kinetic first order is observed. At high coverage, the satura-

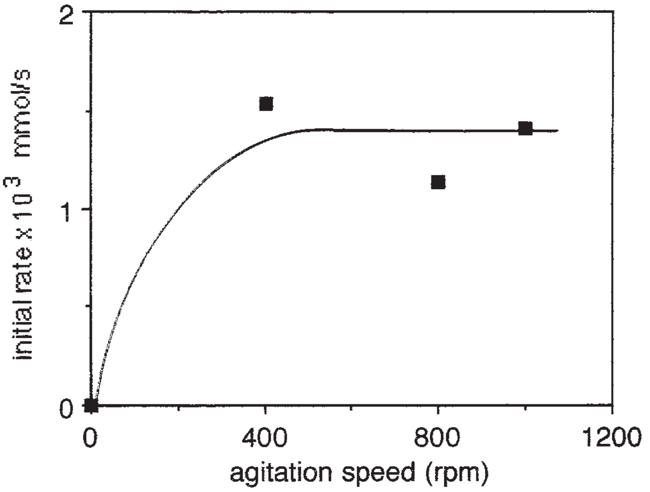

Figure 1. Effect of the agitation speed on the initial hydrolysis rate of methyl α-D-glucopyranoside.

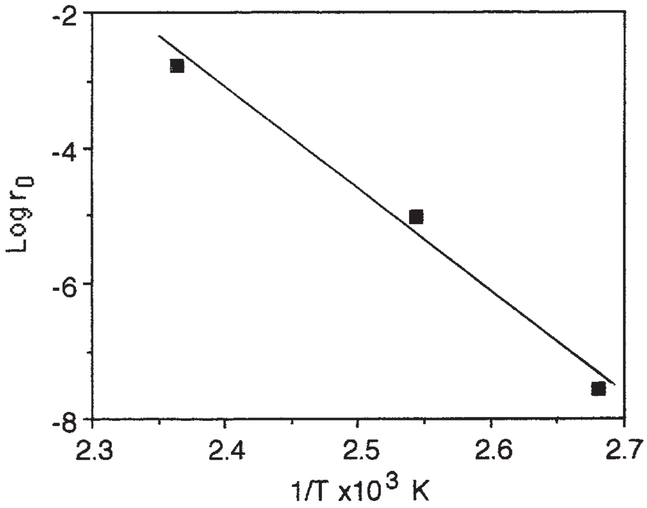

Figure 2. Arrhenius plot for hydrolysis of methyl α-D-glucopyranoside.

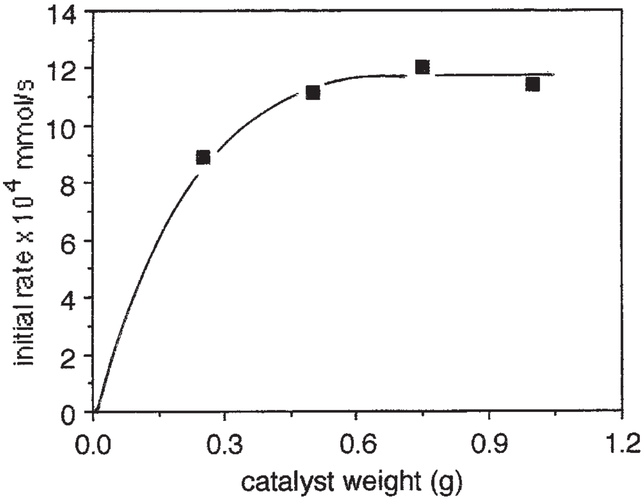

Figure 3. Plot of initial hydrolysis rates against catalyst weight for methyl α-D-glucopyranoside.

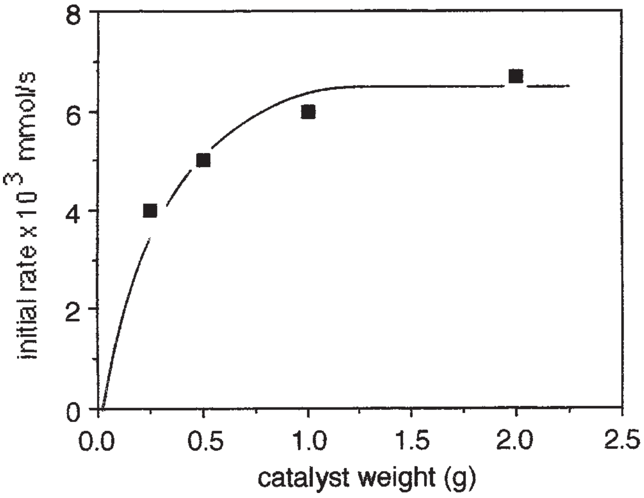

Figure 5. Plot of initial hydrolysis rates against catalyst weight for methyl β-D-glucopyranoside.

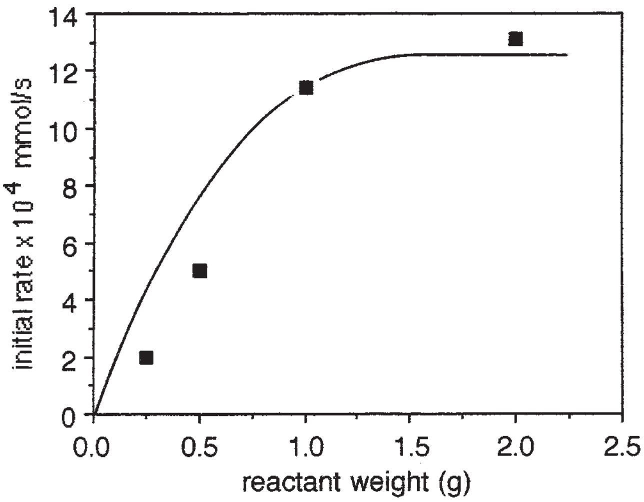

Figure 4. Plot of initial hydrolysis rates against reactant weight for methyl α-D-glucopyranoside.

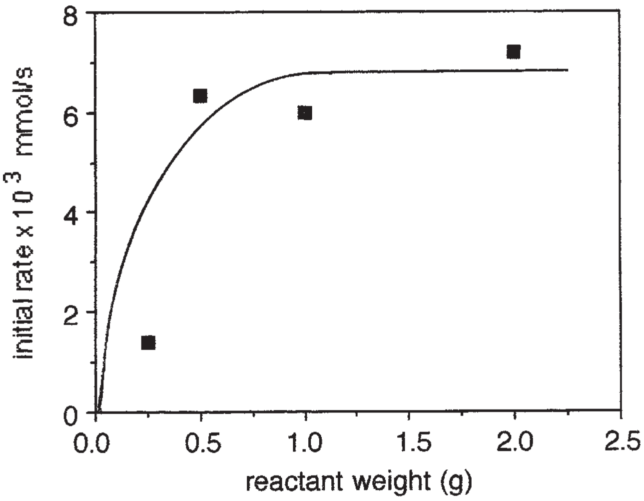

Figure 6. Plot of initial hydrolysis rates against reactant weight for methyl β-D-glucopyranoside.

tion of the catalyst occurs and a zero-order is then observed. These kinetic orders are confirmed in the plot of the initial reaction rates against glycoside concentration (figure 4), and from both figures it is possible to calculate the maximum value of the reaction rate, i.e., about 11–12 $\times 10^{-7}$ mol s^{-1}. Such a behavior observed when plotting the initial reaction rates against catalyst weight or initial reactant concentration has already been considered in reactions catalyzed by solids in terms of close analogy with the Michaelis–Menten mechanism operating in enzymatic reactions with the formation of an enzyme–substrate complex [7];

(iv) Similar conclusions can be drawn from the plots of initial reaction rates for hydrolysis of methyl β-D-glucopyranoside as a function of catalyst weight (figure 5) and initial concentration in reactant (figure 6). From both figures it is then possible to calculate the maximum value of the reaction rate, i.e., about 60–70 $\times$ 10^{-7} mol s^{-1}.

The importance of internal diffusion can be estimated from the equation proposed by Weisz [8]: $\mathrm{d}N/\mathrm{d}t \times 1/C_0 \times R^2/D_{\text{eff}} < 0.1$, where $\mathrm{d}N/\mathrm{d}t$ is the reaction rate (mol/(s g)), C_0 is the initial reactant concentration (mol/cm^3), R is the particle radius (cm) and D_{eff} is the effective diffusivity coefficient (cm^2/s). With a maximum reaction rate of 70×10^{-7} mol/(s g), an initial concentration of 1.5×10^{-4} mol/cm^3 and a mean particle radius of 15×10^{-4} cm, there is no limitation by internal diffusion if D_{eff} is greater than 10^{-7} cm^2/s, a reasonable value for the diffusivity coefficient of liquids in microporous systems.

4. Discussion

All these aspects, kinetics, reaction mechanisms, seem to indicate that the reaction is not controlled by external diffusion nor by internal diffusion. The higher β/α hydrolysis rate ratio observed in this work compared to the homogeneous catalyzed reaction is thus mainly due to the presence of the solid catalyst. Methyl β-D-glucopyranoside reacts

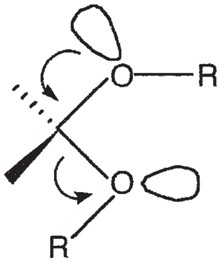

Figure 7. Stabilizing effect (anomeric effect).

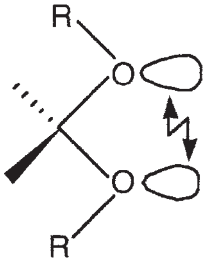

Figure 8. Destabilizing effect (rabbit ear effect).

about 5–6 times faster than the α-anomer, and the β/α ratio is higher than for the homogeneous catalyzed reaction by a factor of about 2–3. This would mean that the effects invoked to account for the homogeneous reaction are still valid, but with an additional effect increasing the reactivity of methyl β-D-glucopyranoside or decreasing the reactivity of methyl α-D-glucopyranoside. Indeed, a higher reactivity of the β-anomer could have been expected because of the possible steric hindrance to accessibility of the α-anomer to the intracrystalline network. But, we have recently shown that for hydrolysis of disaccharides such as maltose (α-linkage) and cellobiose (β-linkage), the α/β ratio is also increased in the presence of a solid catalyst compared to the reaction in solution, 2.8 and 1.5, respectively [2]. Taking into account the tridimensional structure of the Y-faujasite catalyst with an internal diameter of 7.4 Å in all directions and the presence of large cavities of 13 Å of diameter, methyl β-D-glucopyranoside can find place enough to react within the channels or cavities, and can also adopt, as in solution, a twist-boat conformation favorable to stereoelectronic assistance of the kind proposed by Deslongchamps. For more rigid systems such as cellobiose, maltose or other model compounds, there is no conformational change and α-anomers are more reactive.

If shape-selectivity properties of that kind of zeolites cannot fully account for the reactivity in hydrolysis of methyl α- and β-D-glucopyranosides, the higher β/α rate ratio might have the same origin as we have already proposed in hydrolysis and hydrogenolysis of cyclic and acyclic acetals [1]. The rate enhancement observed in hydrolysis of a cyclic acetal such as 2-phenyl-1,3-dioxolane compared to the acyclic one benzaldehyde diethylacetal would result from a better adsorption of the former than for the latter, other things being equal. Indeed, if we consider the origin of the anomeric effect, this effect may be regarded either as a stabilizing effect (figure 7) when an oxygen electron lone pair is antiperiplanar to the other C–O bond (stereoelectronic effect), or as a destabilizing effect (figure 8) because of the interaction between oxygen electron lone pairs (rabbit ear effect). In this latter case, it would then be possible to reduce or to annihilate this destabilizing effect if the interaction occurs with an electron-deficient surface. Such an assumption is preferred since in agreement with both stereoelectronic effects and basic principles of heterogeneous catalysis. Furthermore, the consequences of the favorable orientation of the electron lone pair(s) are an increase of the length of the C–O leaving group which becomes easier to be broken, and an increase of the basicity of the leaving group, leading to both easier protonation and adsorption of oxygen on an electron-deficient surface.

5. Conclusion

The experimental results reported illustrate that mechanistic concepts developed in homogeneous catalyzed reactions can apply, once again, to reactions catalyzed by solids. In the present work, thus is confirmed the importance of adsorption phenomena in hydrolysis of alkyl-D-glucopyranosides, leading to a reinforcement of stereoelectronic effects due to the favorable interaction of oxygen electron lone pairs with the electron-deficient species present on the surface of the solid, protonic species in the case of zeolites.

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