Stereoelectronic effects in hydrolysis and hydrogenolysis of acetals and thioacetals in the presence of heterogeneous catalysts

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Abstract

Hydrolysis of benzaldehyde diethyl acetal, 2-phenyl-1,3-dioxolane and 2-phenyl-1,3-oxathiolane occurs at relatively similar rates in the presence of acidic zeolites compared to the large difference observed in solution. A similar behavior is again observed with the corresponding acetals and thioacetals of furfural. In a similar way, hydrogenolysis of benzaldehyde diethyl acetal, 2-phenyl-1,3-dioxolane and 2-phenyl-1,3-oxathiolane also occurs at relatively similar rates in the presence of sulfided catalysts. The weak difference in the observed reaction rates could be interpreted in terms of stereoelectronic effects, i.e. through a most favorable adsorption of cyclic acetals and thioacetals as due to the orientation of their oxygen or sulfur electron lone pairs, thus leading to a better electron transfer to protonic species in the case of zeolites and to anionic vacancies in the case of sulfided catalysts © 1997 Elsevier Science B.V.

*Keywords:* Hydrolysis; Hydrogenolysis; Acetals; Thioacetals; Zeolites; Sulfides

1. Introduction

Stereoelectronic effects have been shown to play an important role in the cleavage of carbon–heteroatom bonds. First experimental evidence was obtained in oxidation of acetals by ozone, where it was shown that oxidation took place only for conformers which had both oxygen atoms with an electron lone pair oriented antiperiplanar to the C–H bond, as it is illustrated in Scheme 1 with the oxidation of models

of α- and β-glycosides [1–3]. β-glycosides **1** were selectively oxidized to the corresponding hydroxy ester **3** through hydrotrioxide intermediate **2**, whereas α-glycosides **4** were found to be unreactive under the same operating conditions.

Stereoelectronic effects were shown later to control also hydrolytic processes, in particular orthoesters, esters, lactones, amides and lactames hydrolysis [4,5]. These aspects were reviewed by Deslongchamps [6] and Kirby [7]. More recently, hydrolysis of acetals was revisited in order to account for the apparent contradictions observed in the rates of hydrolysis of

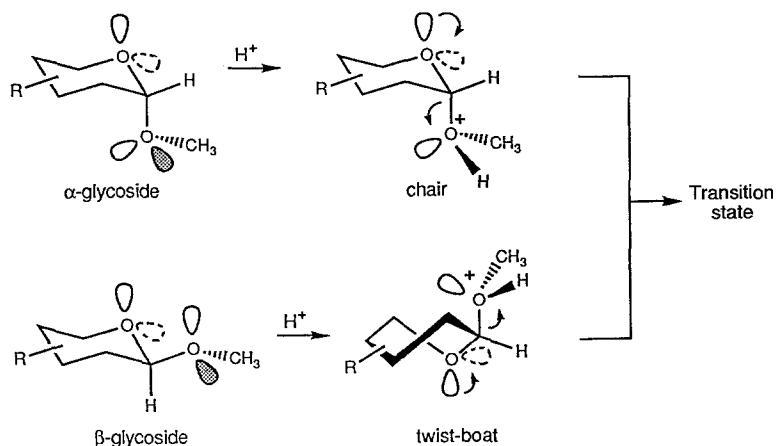* Corresponding author. Tel.: +33-467144320; fax: +33-467144349; e-mail: cmoreau@cit.enscm.fr.
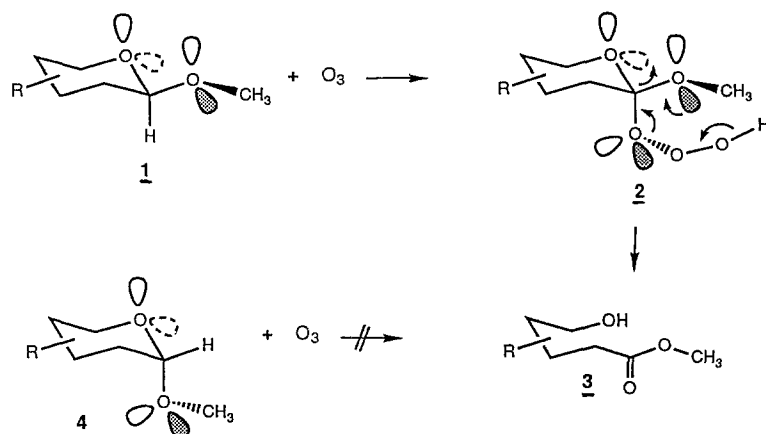
Scheme 1. Stereoelectronic requirements for homogeneous oxidation of models of α- and β-glycosides by ozone.

α- and β-glycosides [8]. In fact, from a study on model compounds, those results were explained in terms of stereoelectronic effects by the difference in energy between ground state and transition state conformations [9]. 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 2.

All these results were obtained under homogeneous catalysis conditions. It was thus possible to consider how stereoelectronic effects can apply to heterogeneously catalyzed reactions involving carbon–heteroatom bonds cleavage, namely hydrolysis and hydrogenolysis of acetals and thioacetals.

In a previous work [10], it has been shown that hydrolysis of acetals like benzaldehyde diethyl acetal and 2-phenyl-1,3-dioxolane occurred at relatively similar rates in the presence of acidic zeolites, compared to the large difference observed in solution [11]. Those results allowed the determination of the Brönsted acidity of a series of solid catalysts under working conditions [12], but the possibility for the orientation of electron lone pairs of those acetals to

Scheme 2. Stereoelectronic requirements for homogeneous hydrolysis of models of α- and β-glycosides.

Benzaldehyde diethyl acetal

2-Phenyl 1,3-dioxolane (X=O)
2-Phenyl 1,3-oxathiolane (X=S)

Furfural diethyl acetal

2-(2-Furyl) 1,3-dioxolane (X=O)
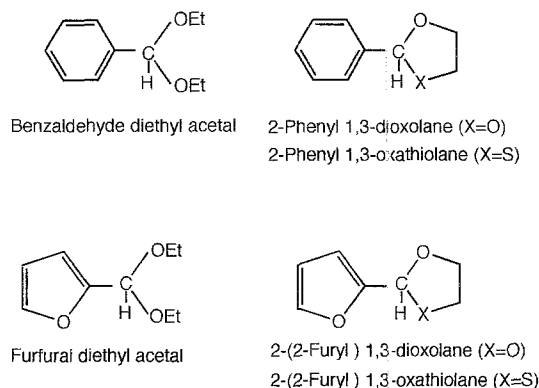2-(2-Furyl) 1,3-oxathiolane (X=S)

Fig. 1. Acetals and thioacetals models of benzaldehyde and furfural.

play a role on the reaction rates was already considered.

The aim of this work was then to investigate further on this latter aspect in reactions involving acetals and thioacetals of benzaldehyde and furfural (Fig. 1), namely hydrolysis in the presence of H-form zeolites, and hydrogenolysis in the presence of sulfided catalysts.

2. Experimental

2.1. Materials

Acetals and thioacetals were synthesized from the corresponding aldehydes available commercially (Aldrich), and according to standard procedures reported in the literature [11].

2.2. Catalysts

Appropriate diluted hydrochloric solutions were used for homogeneous hydrolysis reactions. For heterogeneous hydrolysis reactions, two dealuminated H-mordenites were used, the first one with a Si/Al ratio of 11.1 (benzaldehyde derivatives) and the other one with a Si/Al ratio of 49 (furfural derivatives). Both catalysts were obtained from Zeocat.

The alumina supported cobalt–molybdenum catalyst was Procatalyse HR 306 which has the

following composition: 3% CoO, 14% MoO_3, and 83% γ-Al_2O_3. It was sulfided at atmospheric pressure using a fluidized-bed technique with a gas mixture of 15% H_2S and 85% H_2 by volume. The catalyst (particle size 0.063–0.125 mm) was heated in flowing H_2/H_2S (gas flow, 120 ml/min) from 20 to 400°C (8°C/min) and held at 400°C for 4 h, then cooled, and finally swept with nitrogen for 30 min.

2.3. Hydrolysis experiments in the presence of zeolites

Reaction kinetics were followed by UV spectrophotometry (Gilford 250) by recording the increase in optical density due to the formation of the aldehyde at the corresponding λ_{max} as a function of time. The procedure was as follows. A weighted amount of powder was dispersed in 40 ml of deionized water in thermostated flask (25°C) under stirring and 10 μl of pure acetal were added to this solution. An aliquot of filtered solution was continuously fed into a 100 μl recirculating UV cell using a volumetric pump and the optical density was recorded versus time.

The rate constants were deduced from the experimental plots by curve fitting and simulation using a pseudo-first order kinetic model: $D = D_{inf} + (D_{inf} - D_0)e^{-kt}$, where D_{inf} and D are the optical densities at infinite and t times respectively, D_0 is the optical density at zero tim, and k is the observed rate constant.

2.4. Hydrogenolysis experiments in the presence of sulfides

Hydrogenolysis experiments were carried out in a 0.3 l stirred autoclave (Autoclave Engineers Magne-Drive), working in the batch mode and equipped with a system for sampling of liquid during the course of the reaction without stopping the agitation.

The procedure was typically as follows. A 0.1 M solution of organic reactant in decane or

dodecane (80 ml) was poured into the auto-clave. The sulfided catalyst (0.3 g) was rapidly added to this solution under nitrogen to avoid contact with air. After it had been purged with nitrogen, the temperature was increased under nitrogen until it reached 373 K. Nitrogen was then removed and hydrogen was introduced at the required pressure (4 MPa). Zero time was taken to be when the agitation began (700 rpm).

Analyses were performed on a Delsi 200 gas chromatograph equipped with a flame ionization detector using hydrogen as carrier gas, and capillary columns (Chrompack CP Sil 5 CB or CP Sil 19 CB, 25 m × 0.22 mm i.d.). Products were identified by comparison with authentic samples and GC–MS analyses.

The rate constants were deduced from the experimental plots by curve fitting and simulation, assuming all the reactions to be first order in the organic reactant.

Under the operating conditions reported, hydrolysis and hydrogenolysis reactions were not controlled by external or internal diffusional limitations.

3. Results and discussion

3.1. Hydrolysis of acetals and thioacetals of benzaldehyde

Relative hydrolysis rates of acetals and thioacetals of benzaldehyde obtained in water as the solvent at 298 K are reported in Table 1 for homogeneous and heterogeneous catalyzed reactions.

Table 1
Relative hydrolysis rates of acetals and thioacetals of benzaldehyde

Acetals	Homogeneous	Heterogeneous
2-phenyl-1,3-dioxolane	1 [a]	1 [b]
2-phenyl-1,3-oxathiolane	7.5×10^{-4}	0.6
Benzaldehyde diethyl acetal	39	5

[a] $k_{obs} = 1.23$ s^{-1} g$_{cat}^{-1}$ (HCl 0.68 M).
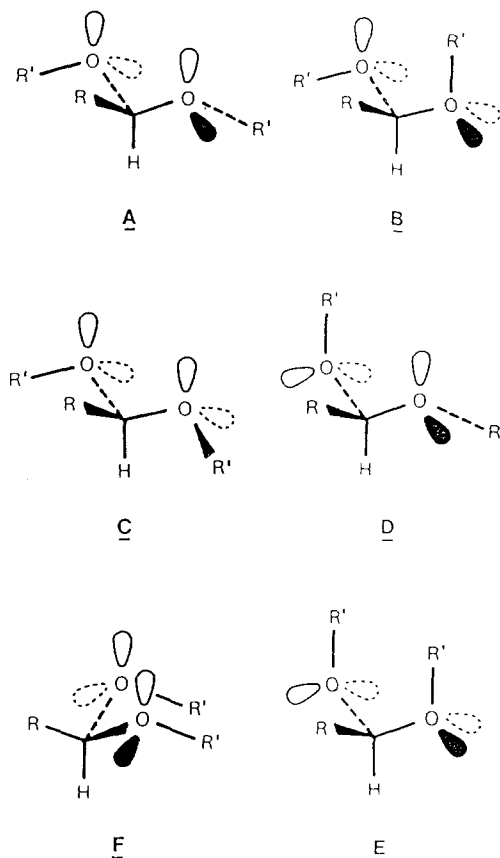[b] $k_{obs} = 0.16$ s^{-1} g$_{cat}^{-1}$ (H-mordenite, Si/Al = 11).

Fig. 2. Illustration of the six different conformations of an acetal.

In a general manner and for reactions catalyzed by homogeneous catalysts, acetals are readily hydrolyzed provided that one oxygen atom has an electron lone pair oriented antiperiplanar to the leaving group. These conditions are fulfilled for most of the six possible conformers which represent acetals in their different forms (Fig. 2). Conformer **A** is the stable model of β-glycosides with one gauche interaction and one anomeric effect. Conformer **B** has two gauche interactions and one anomeric effect. Conformer **C** has only two gauche interactions and conformer **D** is the stable model of α-glycosides with one gauche interaction and two anomeric effects. Finally, conformer **E** is the stable model of 1,3-dioxolanes and 1,3-dioxanes with the substituent R in an equatorial position, whereas this position is axial in con-

2-Phenyl 1,3-dioxolane   Benzaldehyde diethyl acetal (α)   Benzaldehyde diethyl acetal (β)
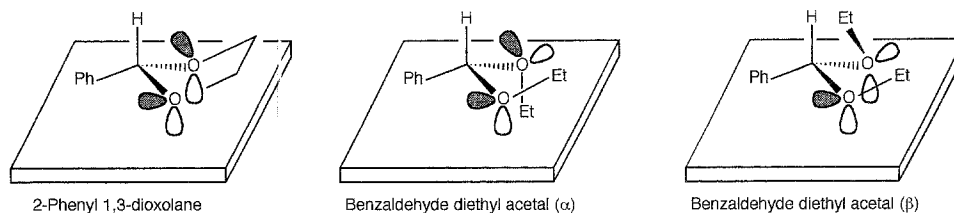
Fig. 3. Stable conformations of 2-phenyl-1,3-dioxolane and benzaldehyde diethyl acetal.

former **F**. Taking into account gauche interactions between R and R' groups and anomeric effects, the increasing order of stability for acyclic acetals is the following: **D > A > B > C**. It is thus seen that 2-phenyl-1,3-dioxolane and benzaldehyde diethyl acetal in its α- or β-form can be hydrolyzed under stereoelectronic control (Fig. 3). The lower reactivity of the cyclic acetal is normally explained by entropic reasons due to ring opening.

In a similar way, 2-phenyl-1,3-oxathiolane fulfills the stereoelectronic requirement of the antiperiplanar orientation with respect to the leaving group. However, the S-containing acetal reacts much more slowly and its lower reactivity was indicating of sulfur protonation prior to the rate-determining cleavage of the protonated C–S bond leading to the oxocarbonium intermediate (Scheme 3) [11].

For the reaction catalyzed by zeolites, the situation is different since the reaction takes place on the surface of a solid, and adsorption is an important parameter to be taken into account. The rate of hydrolysis of benzaldehyde diethyl acetal in its most stable α-form (Fig. 3) may be seen as lowered compared to the rate of hydrolysis of 2-phenyl-1,3-dioxolane. That would be the result of a steric hindrance to adsorption onto the catalyst surface. An alternative explanation, but with exactly the same consequences, is that benzaldehyde diethyl acetal reacts through its less stable β-form (Fig. 3). Due now to the two well oriented electron lone pairs of the heteroatoms, thus favoring both adsorption and accessibility to the protonic sites, such a β-form could not be ruled out. Indeed, that would also account for the small differences observed in the hydrolysis rates of benzaldehyde diethyl acetal, 2-phenyl-1,3-dioxolane and 2-phenyl-1,3-oxathiolane over solid catalysts.

This last explanation would be preferred since in agreement with both stereoelectronic effects and basic principles of heterogeneous catalysis. The consequences of the favorable orientation of the electron lone pair(s) are an increase of the length of the C–heteroatom leaving group which becomes easier to be broken, and an increase of the basicity of the leaving group, leading to

2-phenyl 1,3-dioxolane

2-phenyl 1,3-oxathiolane
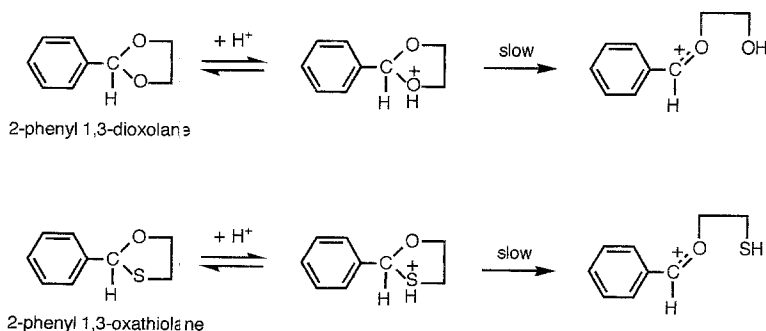
Scheme 3. Protonation step for hydrolysis of 2-phenyl-1,3-dioxolane and 2-phenyl-1,3-oxathiolane.

Table 2
Relative hydrolysis rates of acetals and thioacetals of furfural

Acetals	Homogeneous	Heterogeneous
2-(2-furyl)-1,3-dioxolane	1 [a]	1 [b]
2-(2-furyl)-1,3-oxathiolane	5×10^{-3}	0.3
Furfural diethyl acetal	15	2

[a] $k_{obs} = 8 \times 10^{-3}$ s^{-1} g$_{cat}^{-1}$ (HCl 1.4×10^{-3} M).
[b] $k_{obs} = 9 \times 10^{-4}$ s^{-1} g$_{cat}^{-1}$ (H-mordenite, Si/Al = 49).

both easier protonation and adsorption of the heteroatom on an electron deficient surface.

Furthermore, this explanation would be in line with some results reported in the literature concerning hydrogenolysis of isomeric dihydroxybenzenes on oxide catalysts where the geometries of the substrates and their ability to adsorb on the catalyst surface were shown to play a central role [13].

3.2. Hydrolysis of acetals and thioacetals of furfural

Table 2 reports the experimental results obtained concerning hydrolysis of acetals and thioacetals of furfural in operating conditions similar to those used for hydrolysis of acetals and thioacetals of benzaldehyde. The results reported in this table do not deserve further comments as far as the parallelism in the results reported in Tables 1 and 2 is quite obvious.

3.3. Hydrogenolysis of acetals and thioacetals of benzaldehyde

The results concerning hydrolysis of acetals and thioacetals of benzaldehyde and furfural can
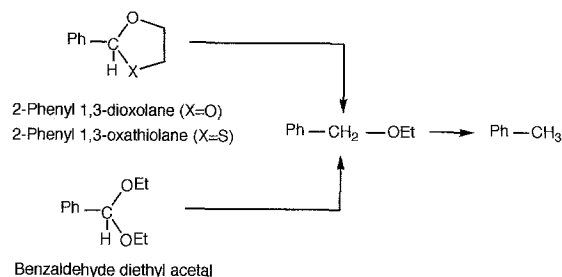

Fig. 4. Kinetic reaction scheme for hydrolysis of acetals and thioacetals of benzaldehyde.

then take some sense as far as a similar situation was observed for the hydrogenolysis of acetals and thioacetals of benzaldehyde over sulfided catalysts (Table 3).

Under the operating conditions used, the reaction proceeds through the formation of benzyl ethyl ether as intermediate, the final product being toluene (Fig. 4). The mechanism proposed for the cleavage of C–O and C–S bonds in the presence of hydrogen, over that kind of catalysts, was first an electron transfer from the heteroatom to an anionic vacancy present on the surface of the catalyst, followed by a hydride transfer from the metal to the carbon atom (Fig. 5) [14,15].

From Table 3 it is then seen that, as for hydrolysis of acetals and thioacetals of benzaldehyde and furfural over solid acids, no large difference in the reaction rates is observed for hydrogenolysis of acetals and thioacetals of benzaldehyde over sulfided catalysts. This result was not unexpected since it is known that the cleavage of a C–S bond is favored over that of a C–O bond in the presence of sulfided cata-

Table 3
Relative hydrogenolysis rates of acetals and thioacetals of benzaldehyde

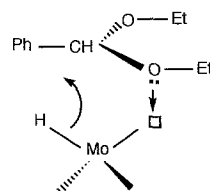| Acetals	Hydrogenolysis
2-phenyl-1,3-dioxolane	1
2-phenyl-1,3-oxathiolane	2.2
Benzaldehyde diethyl acetal	6

Fig. 5. Mechanism of hydrogenolysis of C–heteroatom bonds over sulfided catalysts.

lysts, particularly when they are promoted by cobalt [15]. In addition, hydrogenolysis of isomeric dihydroxybenzenes on sulfided catalysts was again accounted for in terms of geometries of the substrates and their ability to adsorb on the catalyst surface [16].

4. Conclusions

The experimental results reported illustrate once again that mechanistic concepts developed in homogeneous catalyzed reactions can readily apply to reactions catalyzed by solids as it was now well demonstrated for a wide series of reactions [17].

In the present work, it is thus reported the first attempt to show how stereoelectronic effects, largely involved in cleavage of C–heteroatom bonds, can apply to reactions taking place on the surface of a solid. These effects were shown to operate in a classical manner on a molecular standpoint, but they are reinforced due to the favorable interaction of heteroatoms electron lone pairs with the electron deficient species present on the surface of the solid, protonic species in the case of zeolites and anionic vacancies in the case of sulfided catalysts.

References

[1] P. Deslongchamps, C. Moreau, Can. J. Chem. 49 (1971) 2465.

[2] P. Deslongchamps, C. Moreau, D. Fréhel, P. Atlani, Can. J. Chem. 50 (1972) 3402.

[3] P. Deslongchamps, P. Atlani, D. Fréhel, A. Malaval, C. Moreau, Can. J. Chem. 52 (1974) 3671.

[4] P. Deslongchamps, R. Chênevert, R.J. Taillefer, C. Moreau, J.K. Saunders, Can. J. Chem. 53 (1975) 1601.

[5] P. Deslongchamps, U.O. Cheriyan, A. Guida, R.J. Taillefer, Nouv. J. Chim. 1 (1977) 235.

[6] P. Deslongchamps, in: J.E. Baldwin (Ed.), Stereoelectronic Effects in Organic Chemistry, Organic Chemistry Series, Vol. I, Pergamon Press, Oxford, 1983, and references therein.

[7] A.J. Kirby, The Anomeric Effect and Related Stereoelectronic Effects at Oxygen, Springer Verlag, Berlin, 1983.

[8] S. Li, A.J. Kirby, P. Deslongchamps, Tetrahedron Lett. 34 (1993) 7757.

[9] P. Deslongchamps, Pure Appl. Chem. 65 (1993) 1161.

[10] R. Durand, P. Geneste, C. Moreau, S. Mseddi, Stud. Surf. Sci. Catal. 20 (1985) 319.

[11] T.H. Fife, L.K. Jao, J. Am. Chem. Soc. 91 (1969) 4217, and references therein.

[12] C. Moreau, R. Durand, P. Geneste, S. Mseddi, J. Mol. Catal. A Chemical 112 (1996) 133.

[13] R.K.M.R. Kallury, W.M. Restivo, T.T. Tidwell, D.G.B. Boocock, A. Crimi, J. Douglas, J. Catal. 96 (1985) 535.

[14] C. Moreau, J. Joffre, C. Saenz, P. Geneste, J. Catal. 122 (1990) 448.

[15] C. Moreau, J. Joffre, C. Saenz, J.C. Afonso, J.L. Portefaix, Proceedings of the XIIIth Iberoamerican Symposium on Catalysis, 1992, Vol. II, p. 1261.

[16] J.B. Bredenberg, M. Huuska, P. Toropainen, J. Catal. 120 (1989) 401.

[17] A. Finiels, P. Geneste, C. Moreau, J. Mol. Catal. A Chemical 107 (1996) 385.