Adsorption mode of ethyl pyruvate on platinum: an *in situ* XANES study

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The adsorption of ethyl pyruvate on Pt(111) has been studied by *in situ* XANES measurements in the presence and absence of hydrogen. Depending on the hydrogen and ethyl pyruvate pressure, the C and O K-edge spectra exhibit distinctly different angular dependence. Without hydrogen ethyl pyruvate is oriented preferentially perpendicular to the surface, indicating bonding via the O lone pairs. In the presence of hydrogen the mean orientation is more tilted towards the surface. Likely, ethyl pyruvate also interacts with Pt via its π system under these conditions. The observed angle-dependent shift of the energy of the π^* and σ^* resonances indicates the coexistence of differently adsorbed ethyl pyruvate species. The experimental findings demonstrate the importance of the *in situ* approach for unraveling the adsorption mode of ethyl pyruvate in the enantioselective hydrogenation over cinchona-alkaloid-modified Pt.

Keywords: ethyl pyruvate, *in situ* XANES, enantioselective hydrogenation, platinum

1. Introduction

Enantioselective hydrogenation is an important field in catalysis due to the constantly growing need to produce optically pure chiral compounds, especially as pharmaceuticals, agrochemicals, flavors and fragrances [1]. Among the various methods applied in asymmetric synthesis, catalysis provides the unique advantage of multiplying the chiral information such that a minor amount of catalyst can produce a large amount of optically pure product. For industrial applications a heterogeneous catalyst would be desirable due to advantages over homogeneous catalysts in separation, handling and reuse.

A promising strategy for heterogeneous enantioselective hydrogenation is to modify a metal catalyst with a chiral adsorbate. Two such catalyst systems have been extensively studied [2]: tartaric-acid-modified Ni for the enantioselective hydrogenation of β-ketoesters and 2-alkanones and cinchona-alkaloid-modified Pt for the enantioselective hydrogenation of α-ketoesters. For both systems high enantiomeric excess (ee) up to 90–95% can be achieved, however only for a limited number of substrates. The broadening of the scope of these reactions is highly desirable but hampered by the lack of a thorough understanding of the reaction mechanism and enantio-differentiation.

The enantioselective hydrogenation of ethyl pyruvate has played a key role in the elucidation of the mechanism of enantio-differentiation on cinchona-modified platinum. Several mechanistic models have been proposed and discussed in recent reviews [2–6]. All these models suffer from the constraint that assumptions had to be made concerning the adsorption mode of the modifier and reactant. No *in situ* spectroscopic information is available to date. H/D exchange experiments indicate that cinchonidine interacts with Pt through its quinoline moiety [7]. The catalytic behavior of cinchonidine, where the hydrogen nearest to the quinoline N was substituted by a phenyl group (2-phenyl-9-deoxy-10,11-dihydrocinchonidine), furthermore showed that cinchonidine is not adsorbed through the quinoline N lone pair, indicating flat adsorption via the quinoline π system [8]. Recently an ultrahigh vacuum NEXAFS study has been presented, which corroborates the flat adsorption mode of cinchonidine [9]. Information about the adsorption mode of ethyl pyruvate on platinum is still a missing piece of information in the puzzle, preventing us from having a more complete view of the reaction mechanism and enantio-differentiation. This prompted us to investigate the interaction of ethyl pyruvate with a platinum surface.

XANES (X-ray absorption near edge structure) spectroscopy is ideal to tackle the adsorption mode of ethyl pyruvate for mainly two reasons. Firstly, through angle-dependent measurements direct and unambiguous information about the orientation of a molecule can be obtained without the need for extended data analysis. Secondly, XANES measurements can be performed at relatively high pressure thus enabling *in situ* measurements. This last point is of special importance for our purpose, since it is not *a priori* clear, whether the adsorption mode of ethyl pyruvate is affected by the presence of hydrogen on the Pt surface. Here we present first results on the adsorption of ethyl pyruvate on Pt studied by *in situ* XANES measurements.

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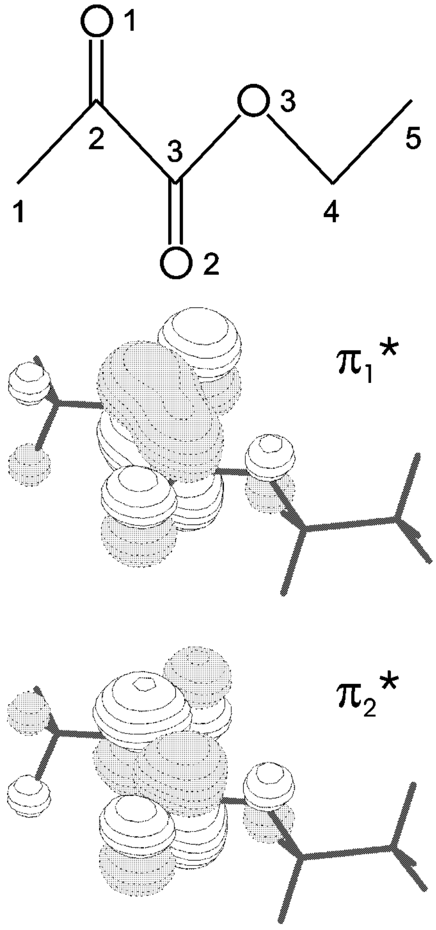
2. Experimental

The experiments were carried out at the beamline HE-TGM1 at the Berliner synchrotron radiation source BESSY-I with an electron beam energy of 0.8 GeV [10]. A toroidal grating monochromator with a resolution of 0.7 eV at the carbon K-edge and a resolution of 2.0 eV at the oxygen K-edge was used. The measurements were performed on a Pt(111) single crystal. The Pt(111) surface was cleaned by Ar^+ bombardment at 3.5 kV with simultaneously heating at 900 K and subsequent annealing at 650 K in 1 mbar H_2 for 10 min. Ethyl pyruvate (Aldrich, 98%) was purified by repeated freeze–pump–thaw cycles. Dosings of H_2 and ethyl pyruvate were done successively by separate leak valves. All measurements were performed *in situ* at room temperature in the batch mode. Angular dependence was investigated by performing measurements at 90° (normal incidence), 45° and 20° (grazing incidence).

The XANES experimental setup is described in full detail elsewhere [11]. Briefly, the apparatus is built up of two UHV chambers separated by a polyimide X-ray window. One chamber serves as a reactor and the second as an interface between the reactor and the beamline of the BESSY storage ring. The polyimide X-ray window allows filling of the reactor with gases up to pressures of 1000 mbar without breaking the vacuum in the second chamber (pressure below 5×10^{-9} mbar). The "interface chamber" is equipped with a conventional monitor for the X-ray intensity, I_0, emitted by the storage ring and the reactor with three detectors, which can be operated simultaneously and independently. They allow to monitor the signals coming from the gas phase (signal I_1), the sample surface related and gas phase (I_2), and the specimen stage (I_3). All XAS data were collected in the total-electron yield (TEY) modus. The treatment of raw XAS data is explained with full details in [11]. The energy scale was calibrated using the π^* resonance of gas-phase CO at 287.4 eV (C-edge) and 534.0 eV (O-edge) as standard.

3. Results and discussion

Ethyl pyruvate (scheme 1) has two π^* orbitals arising from the two C=O double bonds. Due to their proximity one can expect the two π^* orbitals to be delocalized over both C=O double bonds, analogous to the π^* orbitals in butadiene [12]. This delocalization is also shown in scheme 1 where the π_1^* and π_2^* molecular orbitals are depicted as derived from semi-empirical PM3 calculations. As a consequence we expect strong transitions from the C_2, C_3, O_1 and O_2 (scheme 1) 1s orbitals to both π_1^* and π_2^* giving rise to four π^* transitions for each the C K- and the O K-edge. The PM3 calculations give an energy separation of 1.8 eV between π_1^* and π_2^*. The π_1^* wave function has a larger amplitude at the keto group whereas π_2^* is stronger at the carboxyl group. As concerns the electron binding energies, the 1s of the carboxyl C_3 is expected to be stronger bound than the 1s of the keto C_2 by 0.5–1.5 eV [13]. On the other hand, the 1s of O_1 and O_2 are expected to have very similar binding energies [14]. With this information in mind we assign the gas-phase C K-edge XANES spectrum of ethyl pyruvate shown in figure 1(D) as follows: the lowest energy band at 286.3 eV is assigned to the $C_2 \rightarrow \pi_1^*$ transition. Due to the larger binding energy of the 1s electron at C_3 the corresponding $C_3 \rightarrow \pi_1^*$ transition contributes to the band at 288.4 eV overlapping with $C_2 \rightarrow \pi_2^*$. The tail towards higher photon energies of the band at 288.4 eV contains several transitions among which is $C_3 \rightarrow \pi_2^*$. Alternatively we could assign the band at 286.3 eV to $C_2, C_3 \rightarrow \pi_1^*$ and the band at 288.4 eV to $C_2, C_3 \rightarrow \pi_2^*$. This uncertainty in assignment does not affect the conclusions drawn in the following from the angle-dependent band intensities of adsorbed ethyl pyruvate. The bands at 290.0, 291.3 and 298.0 eV arise from σ^*(C–O) and σ^*(C=O) resonances. The assignment of the O K-edge spectrum (figure 2(D)) is less ambiguous. The broad band at 530.7 eV arises from the four transitions $O_1, O_2 \rightarrow \pi_1^*, \pi_2^*$, whereas the band at 542 eV is due to σ^* resonances.



Scheme 1. Ethyl pyruvate atom numbering. The lower part depicts the π_1^* and π_2^* molecular orbitals (PM3 calculation).

The O K-edge spectra of adsorbed ethyl pyruvate measured at different hydrogen and ethyl pyruvate partial pressures and at normal (90°) and grazing (20°) incidence are

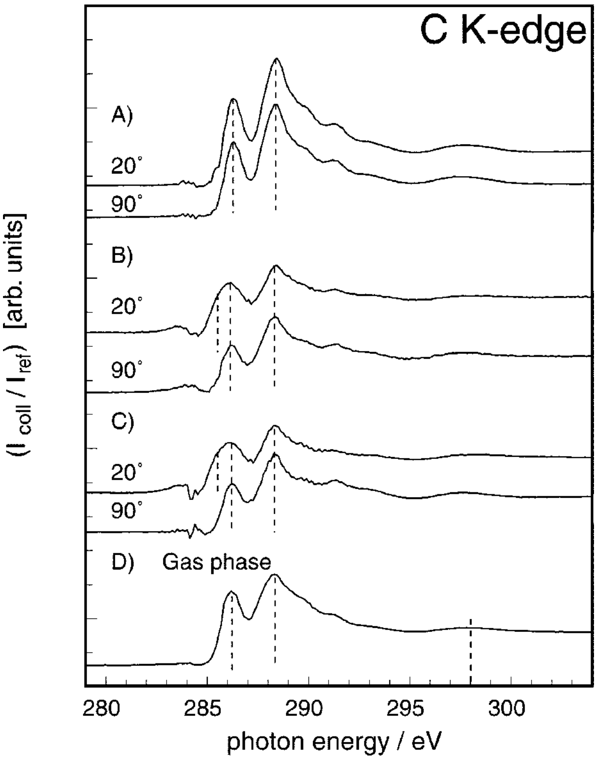


Figure 1. C K-edge XANES spectra of ethyl pyruvate on Pt(111) measured at room temperature at normal (90°) and grazing incidence (20°). The spectra are given as the signal of the actual measurement (I_{coll}) divided by a reference spectrum recorded in Ar atmosphere (I_{ref}), thus accounting for the transmission function of all optical elements. (A) in 0.5 mbar ethyl pyruvate + 0.5 mbar H_2, (B) in 0.11 mbar ethyl pyruvate + 0.5 mbar H_2, (C) in 0.065 mbar ethyl pyruvate and (D) gas phase.

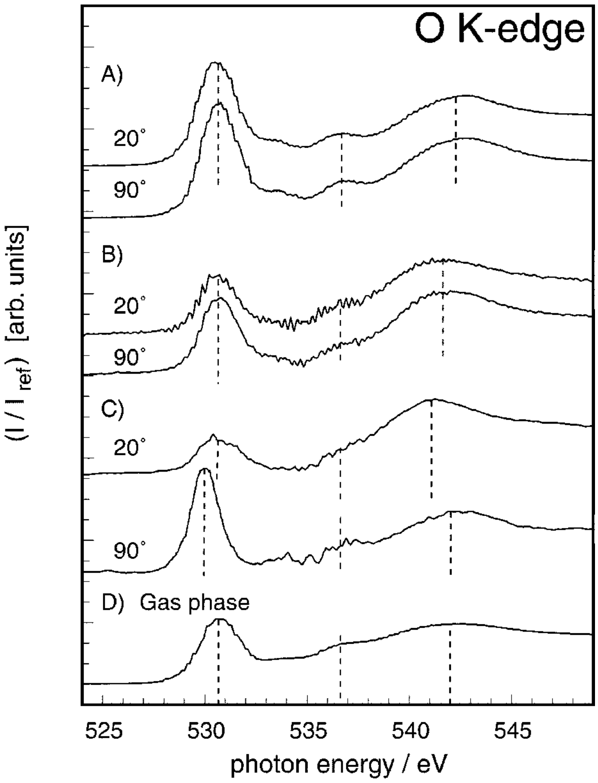


Figure 2. O K-edge XANES spectra of ethyl pyruvate on Pt(111). Experimental conditions identical as for figure 1. The mean tilt angle between the Pt(111) surface and the plane perpendicular to the π^* orbitals (ethyl pyruvate molecular plane) as determined from the intensity of the π^* resonances is (A) 56 ± 5° in 0.5 mbar ethyl pyruvate + 0.5 mbar H_2, (B) 58 ± 6° in 0.11 mbar ethyl pyruvate + 0.5 mbar H_2 and (C) 72 ± 7° in 0.065 mbar ethyl pyruvate.

shown in figure 2. A XANES signal arising from the Pt N-edge was observed at around 520 eV. The strength of this signal was used to estimate the thickness of the adsorbed ethyl pyruvate layer. For low ethyl pyruvate pressure the O K-edge signals show distinct angular dependence arising from a preferred orientation of ethyl pyruvate on the Pt(111) surface. From the relative intensity of the π^* transitions in the O K-edge spectra a mean orientation of the C=O groups can be deduced. The mean tilt angle was determined according to [15]. In the absence of hydrogen (spectrum (C) in figure 2, 0.065 mbar ethyl pyruvate) this angle is determined as 72 ± 7° (18 ± 7° with respect to the surface normal). In the presence of 0.5 mbar hydrogen (spectrum (B) in figure 2) this angle decreases to 58 ± 6° (32 ± 6° with respect to the surface normal). Thus in the presence of hydrogen the mean orientation of ethyl pyruvate is more tilted towards the surface. Although the determination of the mean tilt angle could not be made with highest accuracy, the calculated values unequivocally demonstrate that the orientation of adsorbed ethyl pyruvate is affected by coadsorbed hydrogen. This conclusion already emerges from a comparison of spectra (B) and (C) in figure 2.

At 0.5 mbar ethyl pyruvate partial pressure and 0.5 mbar H_2 (figure 2(A)), on the other hand, no angular dependence can be observed. At the same time the Pt N-edge signal decreases to about 30% of its intensity at low ethyl pyruvate pressure (0.11 and 0.065 mbar ethyl pyruvate: figure 2 (B) and (C)). Under these conditions ethyl pyruvate forms a condensed liquid layer (more than 1 nm thick) in which the individual molecules are randomly oriented.

Apart from the orientation-dependent intensities also the position of the broad band associated with σ^* resonances at 542 eV changes with the experimental conditions. At high ethyl pyruvate pressures (spectra (A) in figure 2) the center of this band is close to the 542 eV observed for gas-phase ethyl pyruvate, as expected for a condensed liquid layer. At lower ethyl pyruvate pressure and in the presence of hydrogen (spectra (B) in figure 2), the center of this band is shifted to lower energy, indicating an increase of the mean C=O bond length, as one would expect for a chemisorbed species. Upon chemisorption some charge is transferred to the antibonding π^* orbitals (back-donation) [16], thus elongating the C–O bond distance. Furthermore, changes in band position can also be observed when changing the angle of incidence. This is most evident for the spectra measured in the absence of hydrogen (spectra (C) in figure 2) but can also be observed in the presence of hydrogen. This last observation is a strong indication for the coexistence of ethyl pyruvate species in different adsorption modes, possibly one oriented preferentially parallel and one preferentially perpendicular to the surface. At normal and grazing incidence the contribution from the different species to the π^* and σ^* spectrum changes due to their different orientation. Specifically, in the spectra (C) (figure 2) the π^* band center shifts to higher photon energy when going from normal to grazing incidence. At normal incidence the species oriented in a more upright position are preferentially observed, whereas at grazing incidence the more flat lying species dominate the π^* spectrum. The observed energy shift therefore shows that the π^* orbitals of the more flat lying species are stabilized with respect to the upright species. This is consistent with an enhanced π^* back-donation for the former species, as expected for a π-bonding mechanism.

Similar behavior can be observed for the C K-edge as described above for the O K-edge. However, at the C K-edge the observed orientation dependence is less pronounced due to some carbon signals from the Pt surface, which are not associated with ethyl pyruvate. These signals were also observed without admitting ethyl pyruvate. The most prominent of these signals is observed at 285.6 eV (partially overlapping with the π^* transitions of ethyl pyruvate at 286.3 eV) and is strongest at grazing incidence (20°). Both energy and angular dependence of this signal indicate a small amount of graphitic carbon present under *in situ* conditions [17]. On the other hand, the band at 288.4 eV associated with π^* transitions in the C-edge spectra is less affected by the signals from graphitic C. This band shows no angular dependence at high ethyl pyruvate partial pressure (figure 1(A)), whereas for low partial pressure (figure 1 (B) and (C)) the band is more intense at 90° than at 20°, similar as observed for the π^* transitions in the O-edge spectra. We note that the observed angular dependence and energy shifts were reproducibly observed for a variety of different ethyl pyruvate and hydrogen partial pressures.

The present *in situ* XANES study qualitatively shows, that the adsorption mode of ethyl pyruvate is influenced by coadsorbed hydrogen. In the presence of hydrogen the mean angle between the molecular plane and the surface is decreasing relative to the situation without hydrogen. This underlines the importance of the *in situ* spectroscopic approach. The data furthermore strongly indicate the coexistence of two differently adsorbed species, possibly lone-pair- and π-bonded ethyl pyruvate, analogously as was found for acetone adsorption on Ru surfaces [16]. In the π-bonded mode the π^* orbitals of the keto group point towards the surface. From a molecular orbital point of view it is therefore reasonable that the hydrogen atoms approaching ethyl pyruvate from below have the highest probability to react with the π-bonded ethyl pyruvate. Such a directionality of approach of the H atom to the π^* orbitals is a prerequisite for enantioselective hydrogenation and has recently also been proposed to be a critical element in the catalytic hydrogenation activity of ethylene and acetylene on Ni(111) [18].

In conclusion, we can state that ethyl pyruvate adsorption is affected by the presence of hydrogen and that lone-pair- and π-bonded ethyl pyruvate possibly coexist on the platinum surface. The present findings indicate that the previously suggested flat π-bonded ethyl pyruvate [5,19] in the relevant enantio-differentiating diastereomeric transition state is feasible, particularly because the hydrogen bonding between the oxygen atom of the α-carbonyl moiety and the quinuclidine N of the coadsorbed cinchonidine should further favor the π-bonded species. In this sense the lone-pair-bonded ethyl pyruvate could be considered as a precursor state of the final π-bonded species, suggested to be relevant in the transition state complex.

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References

[1] A.N. Collins, G.N. Sheldrake and J. Crosby, *Chirality in Industry: The Commercial Manufacture and Applications of Optically Active Compounds* (Wiley, New York, 1995).

[2] A. Baiker and H.U. Blaser, in: *Handbook of Heterogeneous Catalysis*, Vol. 5, eds. G. Ertl, H. Knözinger and J. Weitkamp (VCH, Weinheim, 1997) p. 2422.

[3] A. Baiker, T. Mallat, B. Minder, O. Schwalm, K.E. Simons and J. Weber, in: *Chiral Reactions in Heterogeneous Catalysis*, eds. G. Jannes and V. Dubois (Plenum, New York, 1995).

[4] G.J. Hutchings, J. Chem. Soc. Chem. Commun. (1999) 301.

[5] A. Baiker, J. Mol. Catal. A 115 (1997) 473.

[6] H.U. Blaser, H.P. Jalett, M. Müller and M. Studer, Catal. Today 37 (1997) 441.

[7] G. Bond and P.B. Wells, J. Catal. 150 (1994) 329.

[8] T. Bürgi, Z. Zhou, N. Künzle, T. Mallat and A. Baiker, J. Catal. 183 (1999) 405.

[9] T. Evans, A.P. Woodhead, A. Gutierrez-Soza, G. Thornton, T.J. Hall, A.A. Davis, N.A. Young, P.B. Wells, R.J. Oldman, O. Plashkevych, O. Vahtras, H. Agren and V. Carravetta, Surf. Sci. 436 (1999) L691.

[10] E. Dietz, W. Braun, A.M. Bradshaw and R.L. Johnson, Nucl. Instrum. Methods A 239 (1985) 359.

[11] A. Knop-Gericke, M. Hävecker, T. Neisius and T. Schedel-Niedrig, Nucl. Instrum. Methods A 406 (1998) 311.

[12] D. Coulman, J.L. Solomon, R.J. Madix and J. Stöhr, Surf. Sci. 257 (1991) 97.

[13] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin–Elmer, Eden Prairie, MN, 1979).

[14] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P.F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[15] J. Stöhr, *NEXAFS Spectroscopy* (Springer, Berlin, 1992).

[16] A.B. Anton, N.R. Avery, B.H. Toby and W.H. Weinberg, J. Am. Chem. Soc. 108 (1986) 684.

[17] F. Atamny, J. Blöcker, B. Henschke, R. Schlögl, T. Schedel-Niedrig, M. Keil and A.M. Bradshaw, J. Phys. Chem. 96 (1992) 4522.

[18] K.L. Haug, T. Bürgi, T.R. Trautman and S.T. Ceyer, J. Am. Chem. Soc. 120 (1998) 8885.

[19] O. Schwalm, B. Minder, J. Weber and A. Baiker, Catal. Lett. 23 (1994) 271.