Coadsorption of methyl pyruvate and (±)-1-(1-naphthyl)ethylamine on Pt(111): insights on the mechanism for asymmetric hydrogenation

Stéphane Lavoie, Marc-André Laliberté, and Peter McBreen*

Département de chimie, Université Laval, Québec, Canada

Received 8 May 2004; accepted 19 July 2004

The results of a series of adsorption and coadsorption measurements using (±)-1-(1-naphthyl)ethylamine (NEA), methyl pyruvate, ester-deuterated methyl pyruvate, methyl naphthalene and 2,3-butanedione on Pt(111) are presented. Coadsorption of NEA stabilizes a molecularly adsorbed state of methyl pyruvate. The latter state undergoes thermal decomposition to yield a methane desorption peak centred at 320 K. Experiments performed using ester-deuterated methyl pyruvate show that the methane desorption results from the decomposition of the acetyl moiety of the α-ketoester. A stabilizing interaction is not observed for coadsorbed methyl naphthalene and methyl pyruvate, presumably due to the absence of an amine group. The study provides further evidence for the existence of a 1:1 methyl pyruvate–1-(1-naphthyl)ethylamine docking complex on Pt(111) under ultrahigh vacuum conditions.

KEY WORDS: butanedione; enantioselective catalysis; methyl pyruvate; methylnaphthalene; naphthylethylamine; Pt(111).

1. Introduction

The Orito reaction describes the enantioselective hydrogenation of α-ketoesters on chiral-modified supported platinum catalysts at temperatures close to 320 K [1–3]. The most widely accepted mechanism for the reaction involves the formation of an adsorbed 1:1 modifier–substrate complex. Three recent publications provide insight on inter-adsorbate interaction between chiral modifiers and α-ketoesters [4–6]. First, a scanning tunneling microscopy (STM) study by Bonello *et al.* [4] revealed images consistent with a 1:1 docking complex between 1-(1-naphthyl)ethylamine (NEA) and methyl pyruvate (MP) on Pt(111). Second, independent infrared spectroscopy studies have provided evidence for a H-bonding interaction between cinchonidine and ketopantolactone on Pt/Al_2O_3 [5] and between coadsorbed NEA and MP on Pt(111) [6]. The latter studies also showed evidence that the interaction is accompanied by a change in the adsorption geometry of the modifier. It is worth noting that both studies yielded similar information, despite the fact that they probed surfaces in solution and in ultrahigh vacuum, respectively. This observation is consistent with the report by von Arx *et al.* [7] that solution-phase is not required to carry out the enantioselective reaction. In this Letter, we describe a series of temperature programmed desorption (TPD) studies aimed at probing interactions between coadsorbed MP and NEA on Pt(111).

2. Experimental

The experiments were performed using a standard ultrahigh vacuum system equipped for thermal desorption, reflectance infrared spectroscopy and Auger spectroscopy measurements. The Pt(111) crystal was cleaned by oxygen treatment, argon sputtering and flash anneal cycles to 1100 K. The sample was spot-welded to Ta wires spanning two electrical feedthroughs at the base of a liquid nitrogen dewar. This permitted temperature control over the 96–1200 K range. Methyl pyruvate, (±)-1-(1-naphthyl)ethylamine, methyl naphthalene, 2,3-butanedione (Sigma–Aldrich) and ester-deuterated ($CH_3COCOOCD_3$) methyl pyruvate (CDN Isotopes) were further purified by freeze–thaw cycles. Thermal desorption measurements were made at a heating rate of 0.5 K/s. Reflectance FTIR spectroscopy (RAIRS) were performed using a Bruker VECTOR 22 spectrometer. Spectra were obtained by coadding 1050 scans.

3. Results and discussion

The TPD data shown in figure 1 are for adsorption and coadsorption experiments performed on Pt(111) using MP, ester-deuterated methyl pyruvate (MPD), 1-methylnaphthalene (MN), NEA and 2,3-butanedione (BD). The $m/e = 15$ peaks at 230–280 K for coadsorbed MN and MP (a), MP (c) and coadsorbed NEA and MP (d) are due to molecular desorption of MP. The $m/e = 15$ peaks at ~320 K observed for coadsorbed NEA and MP (d), and BD (e), are due to CH_4 desorption resulting from thermal decomposition of MP and BD, respectively. Adsorption of NEA alone (b) does not yield an $m/e = 15$ peak.

---

*To whom correspondence should be addressed.
E-mail: pmcbreen@chm.ulaval.ca

1011-372X/04/0900–0111/0 © 2004 Plenum Publishing Corporation

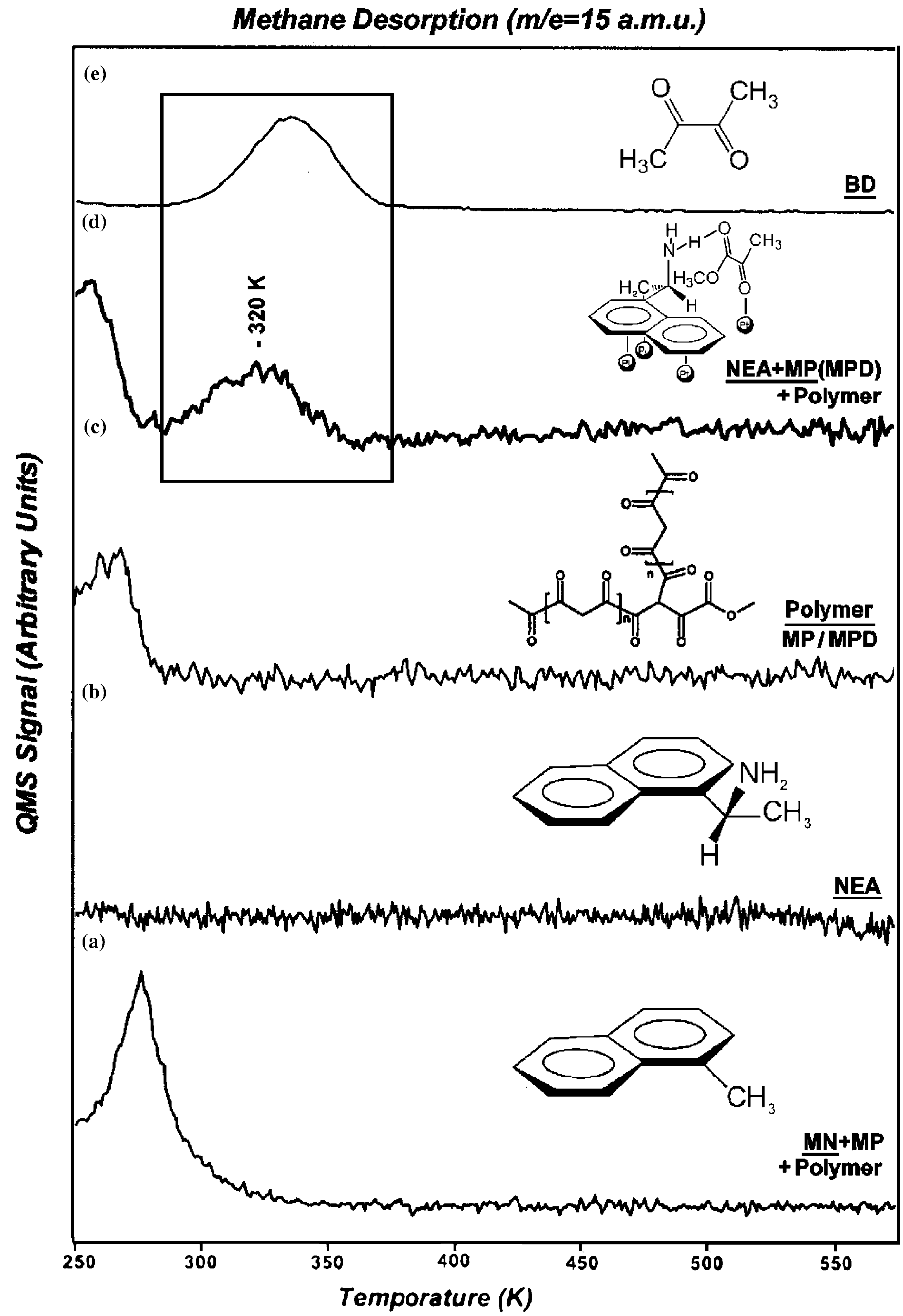


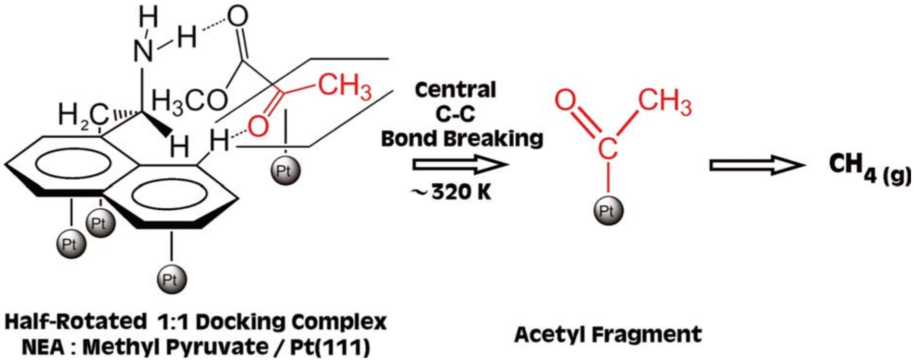
Figure 1. TPD spectra (m/e = 15) for various substrate and modifier–substrate adsorption systems on Pt(111). Exposures were performed at 105 K and the heating rate was 0.5 K/s. (a) coadsorbed methyl naphthalene (MN) and methyl pyruvate (MP); (b) 1-(1-naphthyl)ethylamine (NEA); (c) methyl pyruvate (MP); (d) coadsorbed NEA and ester-deuterated methyl pyruvate (MPD). Coadsorption of MP and NEA yields a an identical desorption spectrum; (e) 2,3-butanedione (BD). The exposures in Langmuir ($1\ L = 1 \times 10^{-6}$ Torr.sec) were (a) 0.2 L MN and 0.3 L MP; (b) 0.3 L NEA; (c) 0.3 L MP; (d) 0.2 L NEA and 0.3 L MP; (e) 0.3 L BD. The illustrations accompanying each spectrum refer only to the underlined species. The surface polymer, a thermal decomposition product of MP is described in papers by Bonello *et al.* [10,11].

Experiments using MPD coadsorbed with NEA also yield desorption spectrum (d) thereby showing that CH_4 desorption arises from the decomposition of the acetyl moiety of methyl pyruvate. This is consistent with the reported decomposition chemistry of acetaldehyde on Pt(111) [8] and stepped Pt(111) [9] surfaces. Acetyl groups on Pt(111), formed through acetaldehyde decomposition, decompose above 300 K leading to CH_4 desorption at 357 K with a shoulder at 320 K [8]. McCabe *et al.* [9] observed a methane desorption peak at 317 K for acetaldehyde on stepped Pt(111). The desorption of methane in the NEA/MP coadsorption experiments is consistent with the presence of MP on the surface to ~320 K, at which temperature dissociation occurs to yield methane desorption via a transient surface acetyl species. Alternatively, dissociation of MP to form a stable acetyl intermediate occurs first, followed by decomposition of acetyl at ~320 K to yield CH_4. In either case, it is clear that NEA increases the thermal stability of adsorbed MP relative to what is observed for the non-modified surface. The weak intensity of the CH_4 peak for coadsorbed NEA/MP, spectrum (d), compared to the intense peak observed for BD, spectrum (e), is consistent with a low coverage of docking complexes in agreement with the STM images reported by Bonello *et al.* [4]

Data for the chemisorption of MP on Pt(111) were reported previously [6]. Briefly, adsorption at 110 K yields a majority enediolate state followed by the formation of η^1-MP close to full-monolayer coverage. Molecular desorption from the η^1-state occurs at 170 K. In contrast, a fraction of the enediolate desorbs as MP at 230–280 K (figure 1(c)) in competition with a surface polymerization reaction first reported and interpreted by Bonello *et al.* [10,11]. The latter authors showed that the polymerization process is inhibited by the presence of coadsorbed hydrogen. The present study shows that NEA also inhibits polymerization, to the extent that a fraction of adsorbed MP is available to undergo the decomposition process leading to methane desorption at 320 K. The inhibition of the polymerization reaction by NEA is a consequence of the stabilization of η^1-MP. Significantly, methane desorption is not observed in experiments performed by coadsorbing MN and MP (figure 1(a)); rather molecular desorption of MP is observed at 230–280 K. NEA and MN are expected to display the same site-blocking effects due to the footprint of the naphthalene ring. Hence, the difference is attributed to the presence of the amine function in NEA. This is consistent with the results of the RAIRS study showing a H-bonding interaction between the amine group of NEA and a carbonyl group of coadsorbed η^1-MP [6], and similar data by Bonalumi *et al.* [5] for the cinchonidine/ketopantolactone coadsorption system. The NEA/MP interaction was found to stabilize η^1-MP on Pt(111) to 320 K [6]. In contrast, MN does not possess an amine function and, as a result, MP desorbs (spectrum 1(a)) at 230–280 K.

The observation of reaction-limited desorption of CH_4 due to the decomposition of an NEA–MP complex may be examined in the context of a previously proposed structure for the docking complex. In the proposed complex [6], MP is η^1-bonded to the platinum surface via the keto-carbonyl group. H-bonding to NEA then occurs via the ester carbonyl. The present study shows that thermal decomposition of the complex does not lead to the desorption of MP but rather scission of the central CC bond occurs to yield surface acetyl followed by reaction-limited desorption of methane. By reference to data for MP on Ni(111) [12,13], scission of the central CC bond while keeping the ester and acetyl moieties of MP intact could also result in the formation of surface methoxycarbonyl. Methoxycarbonyl formation on Pt(111) at ~300 K in the presence of coadsorbed NEA, is confirmed by the comparison of RAIRS data, taken with the sample at 300 K, for Ni(111) [12,13] and Pt(111) [6]. The methoxycarbonyl is characterized by ν(C–O) bands at 1270 and 1268 cm^{-1} and ν(C=O) bands at 1680 and 1677 cm^{-1} for Pt(111) and Ni(111), respectively. Interestingly, methoxycarbonyl formation is observed for MP decomposition on clean Ni(111) and NEA modified Pt(111), but not for clean Pt(111). Ferri *et al.* [14] have reported ATR–IR evidence for the formation of similar carbonyl containing fragments through the dissociation of ethyl pyruvate on clean Pt/Al_2O_3 in CH_2Cl_2.

By analogy to concepts from organometallic chemistry [15] selective activation of the central CC bond of MP requires proximity of the CC bond to the surface. As illustrated in scheme 1, we propose that proximity can be achieved through half-rotation of MP while the entire molecule is attached to the modified surface via H-bonding of the ester carbonyl to NEA. This proposal is made on the basis of the observation of H-bonding between MP, either condensed or chemisorbed, and adsorbed NEA [6]. Rotation of the CO function toward the ring avoids a repulsive interaction between the methyl group and the ring, and may also lead to a weak H-bonding interaction [16]. By extension, we propose that in the presence of a sufficient coverage of atomic hydrogen, hydrogenation rather than CC scission of the



Scheme 1. Proposed structure leading to the formation of methane from coadsorbed 1-(1-naphthyl)ethylamine and methyl pyruvate on Pt(111).

half-rotated state occurs to yield the corresponding lactate.

Acknowledgement

Support from NSERC Discovery and FQRNT team and equipment grants are acknowledged. S.L acknowledges the receipt of NSERC and FQRNT graduate scholarships.

References

[1] Y. Orito, S. Imai and S. Niwa, J. Chem. Soc. Jpn. (1979) 1118.
[2] M. Studer, H.-U. Blaser and C. Exner, Adv. Synth. Catal. 345 (2003) 35.
[3] M. von Arx, T. Mallat and A. Baiker, Top. Catal. 19 (2002) 75.
[4] J.M. Bonello, F.J. Williams and R.M. Lambert, J. Am. Chem. Soc. 125 (2003) 2723.
[5] N. Bonalumi, T. Bürgi and A. Baiker, J. Am. Chem. Soc. 125 (2003) 13342.
[6] S. Lavoie, M.-A. Laliberté and P.H. McBreen, J. Am. Chem. Soc. 125 (2003) 15756.
[7] M. von Arx, N. Dummer, D.J. Willock, S.H. Taylor, R.P.K. Wells, P.B. Wells and G.J. Hutchings, Chem. Commun. (2003) 1926.
[8] H. Zhao, J. Kim and B.E. Koel, Surf. Sci. 538 (2003) 147.
[9] R.W. McCabe, C.L. DiMaggio and R.J. Madix, J. Phys. Chem. 89 (1985) 854.
[10] J.M. Bonello, R.M. Lambert, N. Künzle and A. Baiker, J. Am. Chem. Soc. 122 (2000) 9864.
[11] J.M. Bonello, F.J. Williams, A.K. Santra and R.M. Lambert, J. Phys. Chem. B 104 (2000) 9696.
[12] M. Castonguay, J.-R. Roy, S. Lavoie, A. Adnot and P.H. McBreen, J. Am. Chem. Soc. 123 (2001) 6429.
[13] M. Castonguay, J.-R. Roy, S. Lavoie, M.-A. Laliberté and P.H. McBreen, J. Phys. Chem. B 108 (2004) 4134.
[14] D. Ferri, T. Burgi and A. Baiker, J. Phys. Chem. B (2004) in press.
[15] B. Rybtchinski and D. Milstein, Angew. Chem. Int. Ed. 38 (1999) 870.
[16] S. Lavoie and P.H. McBreen (submitted for publication).