J|A|C|S
COMMUNICATIONS

Published on Web 12/09/2006

Competitive Chemisorption between Pairs of Cinchona Alkaloids and Related Compounds from Solution onto Platinum Surfaces

Zhen Ma and Francisco Zaera*

Department of Chemistry, University of California, Riverside, California 92521

Received August 15, 2006; E-mail: zaera@ucr.edu

The competitive adsorption of two or more compounds from solution onto solid surfaces defines many chemical issues in chemical separations, soil sciences, electrochemistry, aerosol chemistry, prosthetics, and other fields. In heterogeneous catalysis, it typically controls activity and selectivity. In the specific case of chiral modification of platinum-based hydrogenation catalysts by cinchona alkaloids,[1,2] interesting nonlinear effects have been reported where mixtures of modifiers do not lead to a performance average of that of the individual components but rather to the dominance of one over the others.[3−7] This can be explained by the preferential adsorption of that modifier on the surface. Here we provide direct evidence for such asymmetric adsorption uptake on the basis of in-situ reflection−absorption infrared spectroscopy (RAIRS) measurements.

The experiments were carried out in a cell designed for in-situ RAIRS characterization of adsorbates in liquid−solid interfaces.[8,9] The chemicals were purchased from Aldrich, Acros, or Alfa Aesar, and used as received. Their solubilities in CCl_4 were measured as described before.[10] All adsorption experiments were performed at room temperature and were preceded by hydrogen pretreatments.[11]

The competitive chemisorption of the seven quinoline-derived compounds depicted in Figure 1 was studied systematically at the liquid (CCl_4 solution)/solid (platinum disk) interface. Two types of experiments were carried out. The first tested the displacement of one adsorbate (A) by another (B), and yielded results broadly represented by two groups. One, exemplified by the 6-methoxyquinoline (6-MeO-Q)/cinchonidine (CD) pair in Figure 2a, is characterized by the irreversible displacement of one adsorbed compound by the other. Indeed, the RAIRS obtained under a 6-MeO-Q solution (top trace), with its dominant peaks at 1254 and 1278 cm^{-1} and additional features at 1320, 1389, 1425, 1508, and 1603 cm^{-1}, remains virtually unchanged after flushing with pure CCl_4 (second from top), but completely changes upon exposure to CD (middle), after which new large peaks at 1465 and 1512 cm^{-1} and further vibrations at 1238, 1317, and 1338 cm^{-1} due to adsorbed CD[12] develop. The adsorbed CD then survives subsequent flushing with pure CCl_4 (second from bottom) and, more importantly, 6-MeO-Q solutions (bottom).

In the second group, represented by the data for the Q/L pair in Figure 2b, either compound is capable of displacing the other from the Pt surface. The initial spectrum obtained for adsorbed Q, with its peaks at 1228, 1309, 1383, 1396, 1415, 1498, 1565, and 1600 cm^{-1} (top trace),[13] survives flushing with pure CCl_4 (second from top) but not with a L solution (middle), at which point the spectrum of adsorbed L, with its vibrational features at 1225, 1242, 1290, 1371, 1390, 1414, 1502, 1549, and 1604 cm^{-1} appears.[13] The adsorbed L layer remains on the surface after rinsing with pure CCl_4 (second from bottom), but it is displaced by a fresh solution of Q (bottom). The two adsorbates can be exchanged repeatedly and reversibly this way, as also can any pair from the Q, L, 6-MeO-Q trio.

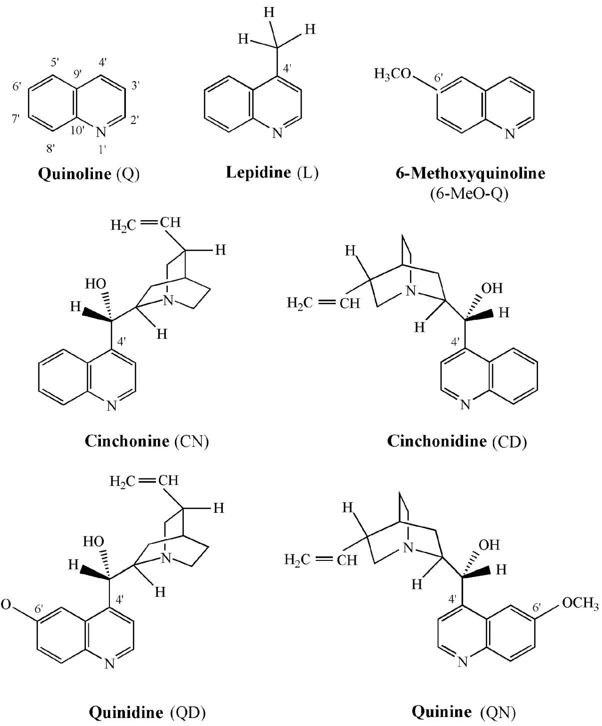

Figure 1. Molecular structures of the seven quinoline-based compounds discussed in this report.

A systematic study following this procedure with all possible pairs using the compounds in Figure 1 led to the following sequence in terms of relative chemisorption strengths: quinine (QN), quinidine (QD) > cinchonidine (CD) > cinchonine (CN) > 6-methoxyquinoline (6-MeO-Q), lepidine (L), quinoline (Q). RAIRS data for additional pairs is provided in the Supporting Information.

The relative chemisorption strength of Q, L, and 6-MeO-Q was established by experiments based on concurrent rather than sequential exposures using mixed solutions of different A/B proportions. Figure 2c summarizes typical infrared spectra obtained for the Q/L pair. Both compounds are detected on the surface with all mixed solutions, even if the adsorption of L is slightly stronger than that of Q. Relative chemisorption strengths were quantified for all possible pairs by using the intensities of representative peaks for each species (1309, 1290, and 1250 cm^{-1} for Q, L, and 6-MeO-Q, respectively) to estimate their surface coverages as a function of their relative concentrations in solution. Those all follow approximately linear trends, a behavior consistent with Langmuir adsorption,[14] and display relative chemisorption constants following 6-MeO-Q/L/Q $\approx$ 4:3:1 ratios.

Relative chemisorption strengths could in principle correlate with melting or boiling points, but a much better indicator turned out to be solubility (Table 1). This fact that can be easily understood by recalling that adsorption can be viewed as a partition between the

10.1021/ja0659323 CCC: $33.50 © 2006 American Chemical Society

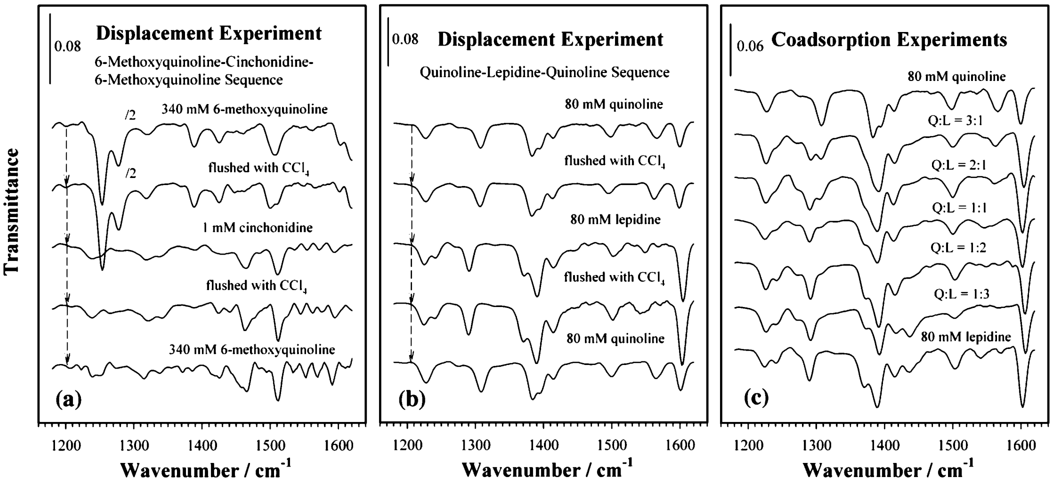

Figure 2. Typical in-situ RAIRS from experiments where a platinum surface was exposed: (a) sequentially to CCl_4 solutions (from top to bottom) of 6-MeO-Q, CD, and back to 6-MeO-Q; (b) sequentially to CCl_4 solutions (from top to bottom) of Q, L, and back to Q; and (c) to mixed Q + L CCl_4 solutions of different compositions. Intermediate flushing with pure CCl_4 were performed in the first two cases to minimize interferences between the two compounds.

Table 1. Melting (T_{mp}) and Boiling (T_{bp}) Points,[18] Solubility in CCl_4 (S), and Onset Concentration for Tilted Adsorption by RAIRS (C_{onset}) for the Quinoline-Derived Compounds in Figure 1

chemical	T_{mp} (K)	T_{bp} (K)	S (g L^{-1})	C_{onset} (mM)
quinoline	256−260	510	∞	2
lepidine	282−283	534−536	∞	1
6-MeO-Q	289	413−419[a]	∞	0.1
cinchonine	531−533		0.090	0.075
cinchonidine	477−479		0.46	0.1
quinine	446−448		2.8	0.05
quinidine	441−445		5.3	0.05

[a] P = 15 Torr.

solution and interfacial phases.[14] It also implies that relative adsorption strengths may be manipulated by choosing appropriate solvents, since the solubilities of cinchona alkaloids vary widely with solvent polarizability.[10] For Q, L, and 6-MeO-Q, which display virtually infinite solubilities in CCl_4, an alternative indicator may be the minimum concentration at which adsorption is detected in the in-situ RAIRS measurements, the values of which are provided in the last column of Table 1. Interestingly, that parameter does not fully follow the order determined for competitive adsorption, as, for instance, CN is detected earlier on the platinum surface than CD even though CD is capable of displacing the adsorbed CN. Note that only tilted adsorption geometries can be detected in our RAIRS experiments and that with the quinoline-based molecules this is preceded by flat-lying species.[15−17] Certainly, high concentrations were used in all experiments to ensure surface saturation and population of the tilted state. There is the expectation for the heats of adsorption to depend on surface coverage, but in this case the trends are likely to be dominated by the adsorption energetics of the aromatic ring, and therefore to be similar with all molecules. Overall, the uptake of the cinchona alkaloids on the platinum surface does appear to be influenced by its coexistence with a second adsorbate.

In summary, it was established by using in-situ RAIRS that, in competitive environments with pairs of solutes, the strengths of adsorption of quinoline-based compounds from CCl_4 solutions onto platinum surfaces follow the sequence: QN, QD > CD > CN > 6-MeO-Q > L > Q. This behavior could be explained at least in part by differences in solubility and may account for nonlinear effects in chiral modification of hydrogenation catalysts such as the dominance of CD in CD + CN mixed solutions[3] and the virtually null effect of adding Q to CD-modified catalysts.[19] A stronger adsorption of CD versus Q was also concluded from electrochemical studies, although some dependence on the structure of the surface was observed there.[20] Interestingly, the higher adsorption strength of QD relative to CD reported here contradicts previous reports.[4,21] It is tempting to try to explain such differences in terms of the different solvents used, except that in all the solvents involved (CCl_4, acetic acid, toluene, and tetrahydrofuran) CD is more soluble than CN.[10] More work is needed to settle this controversy.

Acknowledgment. Funding for this work was provided by the U.S. Department of Energy.

Supporting Information Available: Additional RAIRS from displacement experiments with other cinchona pairs. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Orito, Y.; Imai, S.; Niwa, S. *Nippon Kagaku Kaishi* **1980**, 670.
(2) Baiker, A. *Catal. Today* **2005**, *100*, 159.
(3) Simons, K. E.; Meheux, P. A.; Ibbotson, A.; Wells, P. B. *Stud. Surf. Sci. Catal.* **1993**, *75*, 2317.
(4) Huck, W.-R.; Bürgi, T.; Mallat, T.; Baiker, A. *J. Catal.* **2003**, *216*, 276.
(5) Diezi, S.; Mallat, T.; Szabo, A.; Baiker, A. *J. Catal.* **2004**, *228*, 162.
(6) Balazs, L.; Mallat, T.; Baiker, A. *J. Catal.* **2005**, *233*, 327.
(7) Bonalumi, N.; Vargas, A.; Ferri, D.; Bürgi, T.; Mallat, T.; Baiker, A. *J. Am. Chem. Soc.* **2005**, *127*, 8467.
(8) Kubota, J.; Ma, Z.; Zaera, F. *Langmuir* **2003**, *19*, 3371.
(9) Zaera, F. *Int. Rev. Phys. Chem.* **2002**, *21*, 433.
(10) Ma, Z.; Zaera, F. *J. Phys. Chem. B* **2005**, *109*, 406.
(11) Ma, Z.; Kubota, J.; Zaera, F. *J. Catal.* **2003**, *219*, 404.
(12) Chu, W.; LeBlanc, R. J.; Williams, C. T.; Kubota, J.; Zaera, F. *J. Phys. Chem. B* **2003**, *107*, 14365.
(13) Ma, Z.; Lee, I.; Kubota, J.; Zaera, F. *J. Mol. Catal. A* **2004**, *216*, 199.
(14) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley-Interscience: New York, 1997.
(15) Kubota, J.; Zaera, F. *J. Am. Chem. Soc.* **2001**, *123*, 11115.
(16) Ferri, D.; Bürgi, T. *J. Am. Chem. Soc.* **2001**, *123*, 12074.
(17) LeBlanc, R. J.; Chu, W.; Williams, C. T. *J. Mol. Catal. A* **2004**, *212*, 277.
(18) Lide, D. R., *CRC Handbook of Chemistry and Physics*, 86th ed.; Taylor & Francis, CRC Press: Boca Raton, FL, 2005.
(19) Blaser, H. U.; Imhof, D.; Studer, M. *Stud. Surf. Sci. Catal.* **1997**, *108*, 175.
(20) Fietkaua, N.; Bussara, R.; Baltruschat, H. *Electrochim. Acta* **2006**, *51*, 5626.
(21) Bartók, M.; Sutyinszki, M.; Balázsik, K.; Szöllodblacsi, G. *Catal. Lett.* **2005**, *100*, 161.

JA0659323