clodextrins or even chymotrypsin.[6,10,11] With cyclodextrin, only part of the ester, either the *p*-nitrophenyl or the aliphatic chain, is inserted in the pocket.[12] The apo-Mb cleft is large enough to accommodate the whole ester, at least in the case of **1a** and **1c**, resulting in a binding that is tighter by about 1 kcal. We have made no attempt to optimize the geometry of the transition state by tailoring the substrate to fit the active site. It is therefore conceivable that higher rate accelerations might be achieved with this new semisynthetic esterase.

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(10) Bonora, G. M.; Fornasier, R.; Scrimin, P.; Tonellato, U. *J. Chem. Soc., Perkin Trans. 2* **1985**, 367-369.

(11) Bender, M. L.; Clement, G. E.; Kezdy, F. J.; Heck, H. d'A. *J. Am. Chem. Soc.* **1964**, *86*, 3680-3689.

(12) Breslow, R.; Czarniecki, M. F.; Emert, J.; Hamaguchi, H. *J. Am. Chem. Soc.* **1980**, *102*, 762-770.

Adsorption of Formamide on the Ru(001)-p(1×2)-O Surface: The Spectroscopic Identification of η^2(N,O)-NHCHO

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Despite their importance as prototypes for studying amino acid chemistry, the interaction of amides with well-characterized single-crystalline metal surfaces has not been studied previously. A variety of transition-metal-formamido compounds have been synthesized and characterized, however, and a number of formamide-derived ligands have been observed, including η^1(C)-$CONR_2$ (R = H, alkyl or aryl),[1] η^2(N,O)-NRCRO,[2] η^1(N)-NHC(R)O,[3] η^2(C,O)-NR_2CO,[4] η^2(C,N)-OCNHR,[5] and η^2(C,N)-HOCNH.[6] In this paper, we present preliminary results of an electron energy loss spectroscopic (EELS) and thermal desorption mass spectrometric (TDMS) study of formamide adsorption on the Ru(001) surface on which an ordered p(1×2) overlayer of oxygen adatoms is present. This study provides evidence for the formation of an η^2(N,O)-NHCHO species, analogous to the η^2-formate formed from formic acid decomposition on the initially clean Ru(001) surface.[7,8]

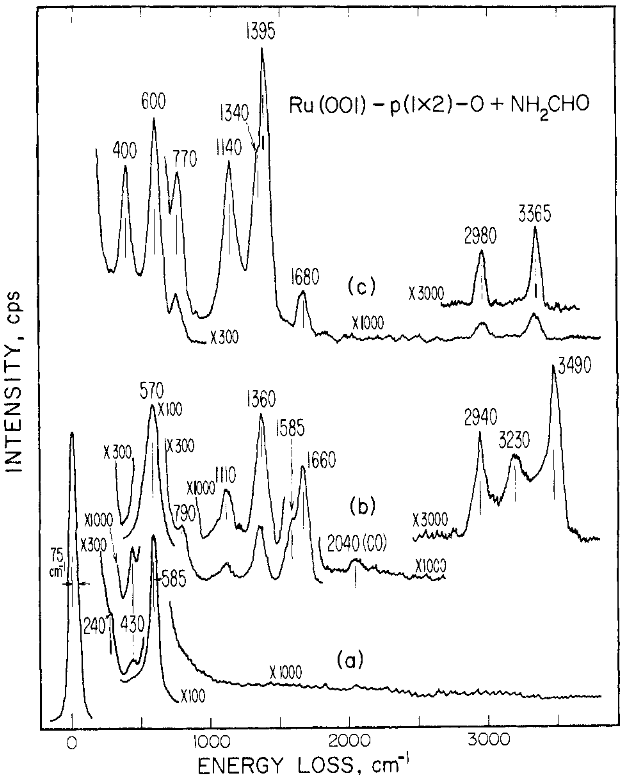

Figure 1. (a) EEL spectrum of the Ru(001)-p(1×2)-O surface. (b) The EEL spectrum that results following a 5×10^{-7} torrs exposure of NH_2CHO to the Ru(001)-p(1×2)-O surface at 80 K, showing the characteristic features of molecular chemisorbed formamide. (c) The EEL spectrum that results when the surface of (b) is annealed briefly to 400 K and recooled to 80 K, showing the characteristic features of η^2(N,O)-NHCHO.

Table I. Vibrational Frequencies in cm^{-1} and Mode Assignments of Molecularly Chemisorbed Formamide on the Ru(001)-p(1×2)-O Surface at 80 K and of Gas-Phase and Liquid Formamide

mode	NH_2CHO/ Ru(001)-p(1×2)-O	NH_2CHO (gas)[13,14]	NH_2CHO (liquid)[13,15]
$\nu_a(NH_2)$	3490	3545	3388
$\nu_s(NH_2)$	3230	3451	3207
ν(CH)	2940	2852	2881
ν(CO)	1660	1734	1681
$\delta(NH_2)$	1585	1572	1611
ν(CN)	1360	1255	1309
δ(CH)	n.o.	1378	1391
π(CH)	n.o.	1030	1050
NH_2 deformations[a]	1110, 790	1059, 602, 289	1090, 750, 200
δ(NCO)	~525[b]	565	595
$\nu(Ru-NH_2CHO)$	310[c]		

[a] The assignment of the NH_2 rocking, wagging, and twisting modes for the molecular formamide is somewhat controversial. thus, we have not attempted to assign these modes. [b] Overlaps with ν_s(RuO) of oxygen adatoms. [c] Not well resolved in Figure 1b; sharpens with annealing. n.o. = not observed, a = asymmetric, s = symmetric.

The ultrahigh vacuum chamber in which the EELS and TDMS experiments were performed has been described previously,[9] as have the properties and method of preparation of the Ru(001)-p(1×2)-O surface.[10-12] The p(1×2)-O overlayer corre-

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[‡] Feodor-Lynen Research Fellow of the Alexander von Humboldt Foundation.

(1) (a) Lindsay, A. J.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1523. (b) Kruse, A. E.; Angelici, R. J. *J. Organomet. Chem.* **1970**, *24*, 231. (c) Sacco, A.; Giannoccaro, P.; Vasapoloo, G. *Inorg. Chim. Acta* **1984**, *83*, 125. (d) Behrens, H.; Vungbauer, A. *Z. Naturforsch., B* **1979**, *34B*, 1477.

(2) (a) Schwering, H.-U.; Weidlein, J. *Chimia* **1973**, *27*, 535. (b) Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Toniolo, L. *Inorg. Chim. Acta* **1983**, *74*, 77. (c) Jennings, J. R.; Wade, K.; Wyatt, B. K. *J. Chem. Soc. A* **1968**, 2535. (d) Adams, R. D.; Golembeski, N, M. *J. Organomet. Chem.* **1979**, *171*, C21.

(3) Burgess, K.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1983**, 1179.

(4) (a) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206. (b) Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243. (c) Mayr, A.; Lin, Y.-C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704. (d) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Mol. Catal.* **1983**, *21*, 297. (e) Azam, K. A.; Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 91.

(5) (a) Kaesz, H. D.; Knobler, C. B.; Andrews, M. A.; van Buskirk, G.; Szostak, R.; Strouse, C. E.; Lin, Y. C.; Mayr, A. *Pure Appl. Chem.* **1982**, *54*, 131. (b) Lin, Y.-C.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1981**, *103*, 1216.

(6) See ref 5a,b. This ligand and the preceding one coexist as a tautomeric mixture.

(7) Toby, B. H.; Avery, N. R.; Anton, A. B.; Weinberg, W. H. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *29*, 317.

(8) Avery, N. R.; Toby, B. H.; Anton, A. B.; Weinberg, W. H. *Surf. Sci.* **1982**, *122*, L574.

(9) Thomas, G. E.; Weinberg, W. H. *Rev. Sci. Instrum.* **1979**, *50*, 497.

(10) Madey, T. E.; Engelhardt, H. A.; Menzel, D. *Surf. Sci.* **1975**, *48*, 304.

(11) Parrott, S. L.; Praline, G.; Koel, B. E.; White, J. M.; Taylor, T N. *J. Chem. Phys.* **1979**, *71*, 3352.

(12) Rahman, T. S.; Anton, A. B.; Avery, N. R.; Weinberg, W. H. *Phys. Rev. Lett.* **1983**, *51*, 1979.

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Table II. Vibrational Frequencies in cm^{-1} and Mode Assignments of η^2(N,O)-NHCHO and η^2(N,O)-NDCHO on Ru(001)–p(1×2)-O[a]

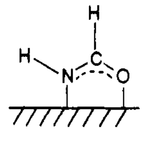
mode	η^2-NHCHO (η^2-NDCHO)	η^2-OCHO[7]	$[R_2MN(CH_3)C(CH_3)O]_2$[2a]
ν(NH)	3365 (2480) w		
ν(CH)	2980 (2960) w	2920 w	
ν_a(NCO)[b]	n.o.	n.o.	1571–1585 at
ν_s(NCO)[b]	1395 (1360) st	1360 st	1392–1400 st
CH bend[c]	1340 (unresolved) sh	n.o.	
NH bend[c]	1140 (920) m		
δ(NCO)[b]	770 (760) m	805 m	n.r.
ν(Ru–NHCHO)[b]	400 (400) st	380 st	355–492 m

[a] s = symmetric, a = asymmetric, st = strong, m = medium, w = weak, sh = shoulder, n.o. = not observed, n.r. = not reported. [b] In the case of η^2-OCHO (formate), the closely related modes are, of course, ν_a(OCO), ν_s(OCO), δ(OCO), and ν(Ru-OCHO), respectively. [c] Since data for CH and NH bending modes in analogous organometallic compounds are lacking, we do not attempt to assign these bending modes as in-plane (δ) or out-of-plane (π).

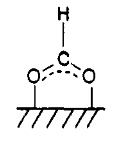
sponds to a fractional coverage of 0.5, and the oxygen adatoms occupy threefold hollow sites on the hexagonally close-packed Ru(001) surface.[11,12] The most notable feature of the EEL spectrum of Figure 1a is the strong mode at 585 cm^{-1} which is due to the symmetric stretching vibration of the oxygen adatoms normal to the surface. The asymmetric ruthenium–oxygen stretch and a ruthenium surface phonon give rise to weaker modes at 430 and 240 cm^{-1}, respectively.[12]

Adsorption of submonolayer concentrations of formamide on the Ru(001)–p(1×2)-O surface at 80 K leads to molecularly chemisorbed formamide, as may be seen from the EEL spectrum of Figure 1b and the mode assignments that are listed in Table I. The fact that the ν(CO), ν(CN), $\delta(NH_2)$, and ν(CH) modes are all present, together with the lack of any modes not due to molecular formamide, indicates that little, if any, dissociation has occurred. The frequencies of the ν(CO) (1660 cm^{-1}) and ν(CN) (1360 cm^{-1}) modes are evidence that no significant rehybridization of these bonds occurs upon adsorption. The slightly lowered frequency of the ν(CO) mode, relative to its gas-phase value of 1734 cm^{-1},[13,14] suggests coordination to the surface via a lone pair of electrons on the oxygen atom, as has been observed for acetone[16] and formaldehyde[17] on Ru(001) surfaces on which ordered overlayers of oxygen are present. The loss feature at 570 cm^{-1} in Figure 1b is broadened because it results from the overlap of two modes: the ν_s(RuO) mode of the oxygen adatoms and the intense δ(NCO) mode of the molecularly adsorbed formamide.[18] The loss feature at 1360 cm^{-1} may involve the in-plane CH bending mode as well as the ν(CN) mode.

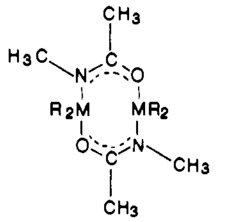
Annealing the Ru(001)–p(1×2)-O surface to 260 K causes the molecularly adsorbed formamide to decompose (which is accompanied by the desorption of H_2[20]), resulting in the formation of a new surface species that is stable to 420 K. This new species is identified by its EEL spectrum (Figure 1c) as η^2(N,O)-NHCHO, the nitrogen-containing analogue of the η^2-formate formed on Ru(001) as the result of formic acid decomposition:[7]



η^2(N,O)-NHCHO



η^2-formate



The η^2(N,O)-NHCHO is also related closely to the $N(CH_3)C(CH_3)O$ ligands in compounds of the type shown at the right, above.[2a] Vibrational data for all of these species are summarized in Table II, and data for η^2(N,O)-NDCHO formed from ND_2CHO decomposition on Ru(001)–p(1×2)-O are presented also. Since η^2(N,O)-NHCHO differs from η^2-formate only in that an oxygen atom has been replaced by an NH group, the skeletal and metal–ligand stretching modes of these two species should occur at very similar frequencies, and it can be seen that this is indeed true for the NCO (OCO) symmetric stretch, the NCO (OCO) scissoring mode, and the metal–ligand stretch.[21] The increase in frequency of δ(NCO) compared with that of the gas-phase formamide (565–770 cm^{-1}) is very similar to the observed increase in δ(OCO) in going from gas-phase formic acid to η_2-formate on Ru(001) (625 to 805 cm^{-1}) and is indicative of delocalized π-bonding within the NCO group. The agreement among the ν_s(NCO) frequencies of η^2(N,O)-NHCHO and the series of (four) $[R_2MN(CH_3)C(CH_3)O]_2$ compounds is clearly excellent. Single CH and NH stretching modes are identified, and no NH_2 scissoring mode is observed at 1500–1600 cm^{-1}. These facts, together with the H_2 desorption near 260 K mentioned above, indicate that one NH bond of the formamide NH_2 group has been cleaved. The EEL spectrum of Figure 1c is thus fully consistent with the presence of an η^2(N,O)-NHCHO species and in excellent agreement with EEL and IR data for closely related surface and organometallic species. Other formamide-derived ligands that have been identified in organometallic compounds[1-6] are inconsistent with the EEL spectrum of Figure 1c for at least one of several reasons: they have no hydrogen atom bonded to the formamide carbon atom; they contain NH_2 groups; they contain CN or CO double bonds (which should give rise to intense stretching modes in the 1500–1800-cm^{-1} region); their δ(NCO) modes should occur at substantially lower frequency. We note finally that we observe no EELS (e.g., ν(OH) or $\delta(OH_2)$ modes) or TDMS (e.g., H_2O desorption) evidence for the formation of OH bonds in this work.

The η^2-NHCHO decomposes when the surface is annealed to 420 K, with reaction-limited CO and H_2 desorbing at this temperature. Nitrogen adatoms remain on the surface to approximately 600 K, at which temperature recombinative desorption of N_2 occurs, leaving the p(1×2)-O overlayer intact. At a saturation coverage of molecularly chemisorbed formamide on the Ru(001)–p(1×2)-O surface, approximately 0.05 monolayer of η^2-NHCHO forms and decomposes.

In summary, formamide chemisorbs molecularly on the Ru(001)–p(1×2)-O surface beow 260 K, in a manner such that the double-bond character of the CO bond is maintained. Annealing the surface to 260 K results in the formation of η^2(N,O)-NHCHO, which decomposes at 420 K. A more detailed account of this work will be presented elsewhere.[19]

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(13) Evans, J. C. *J. Chem. Phys.* **1954**, *22*, 1228.

(14) King, S. T. *J. Phys. Chem.* **1971**, *75*, 405.

(15) Suzuki, I. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1359.

(16) Avery, N. R.; Weinberg, W. H.; Anton, A. B.; Toby, B. H. *Phys. Rev. Lett.* **1983**, *51*, 682.

(17) Anton, A. B.; Parmeter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 1823.

(18) The δ(NCO) mode has been identified unambiguously from EEL spectra of formamide adsorbed on a hydrogen-presaturated Ru(001) surface at 80 K.[19] The same molecularly chemisorbed species is formed, and there is no ν(RuO) mode at 585 cm^{-1} that overlaps with the δ(NCO) mode.

(19) Parmeter, J. E.; Schwalke, U.; Weinberg, W. H., unpublished results.

(20) The amount of H_2 desorbed at 260 K is approximately one-third of the total amount of H_2 that is desorbed as a consequence of the decomposition of formamide on the surface. Any desorption of H_2 from Ru(001)–p(1×2)-O must be reaction-limited because this surface does not chemisorb H_2 under UHV conditions.[17] For sufficiently high initial formamide coverages, some molecular desorption occurs as well.

(21) The ν_a(NCO) mode involves motion of atoms largely parallel to the surface and is apparently very weak and cannot be identified positively. It may contribute to the inensity of the feature at 1680 cm^{-1}. This feature persists to some degree when the surface is annealed to 450 K and the modes due to η^2(N,O)-NHCHO have disappeared. It is due largely or entirely to a very small amount of molecular formamide readsorbed from the chamber background.