J. Am. Chem. Soc. 1992, 114, 4258-4265

Reactions of Unsaturated Oxygenates on Rhodium(111) as Probes of Multiple Coordination of Adsorbates

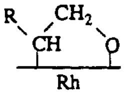
N. F. Brown and M. A. Barteau*

Contribution from the Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716. *Received September 23, 1991*

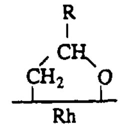
Abstract: The interactions of acrolein, $CH_2{=}CHCHO$, and allyl alcohol, $CH_2{=}CHCH_2OH$, with the Rh(111) surface are dominated at low temperatures by the oxygen function of each molecule. Acrolein is bound initially in an η^2(C,O) configuration; allyl alcohol dissociates to form an allyl alkoxide. For both species, vibrational spectra show significant rehybridization of the olefinic groups upon heating to 200 K and suggest that the surface intermediates are η^4(*C,C,C,O*)-acrolein and η^3(*C,C,O*)-allyl alkoxide. Both intermediates eliminate CO between 200 and 300 K. However, like that of their aliphatic analogues, decarbonylation of acrolein and allyl alcohol does not proceed via a common pathway. Acrolein decomposes to C_2H_6, C_2H_4, CO, H_2, and surface ethylidyne intermediates, but neither allyl alcohol nor any primary alcohol examined on Rh(111) to date produces volatile hydrocarbon products. Thus, although inclusion of the C=C group in these molecules alters the stability of the corresponding surface intermediates, the divergence of reaction pathways for alcohols and aldehydes is unaffected. These results suggest that surface reaction pathways for CO insertion and elimination are considerably more complex than previously recognized.

Introduction

Recent results reported by this laboratory[1-3] and by Friend and co-workers[4-6] have suggested the formation of surface oxametallacycle intermediates in the course of oxygenate synthesis and decomposition reactions on rhodium. These cyclic intermediates are postulated to be of the form



or



If these organic ligands are coordinated to a single surface rhodium atom, the oxametallacycle may be considered structurally analogous to the metallacyclobutanes of importance in reactions such as olefin metathesis.[7] On the extended Rh(111) surface, for which virtually all of this chemistry has been developed to date, coordination to multiple surface rhodium atoms is quite probable, and analogies to five- or six-membered cycles may be more accurate.

One of the remarkable aspects of these yet-to-be-isolated surface oxametallacycles is their apparent importance in a wide range of surface reaction processes. We have suggested previously that they are intermediates in the decarbonylation of primary alcohols[1,2] and epoxides[3] on Rh(111). Friend and co-workers have also invoked them as critical intermediates in reactions on the Rh(111) surface including olefin oxidation to ketones[4] and branched alcohols[5] and the dehydration of *tert*-butyl alcohol.[6] Thus, a wide variety of heterogeneous Rh-catalyzed reactions, from oxidation to hydroformylation, that involve oxygen-containing reactants or products may occur via surface oxametallacycle intermediates.

It has been demonstrated clearly in these and related studies on group VIII metal surfaces that the interaction of aliphatic oxygenates with the surface occurs preferentially at the oxygen function. Alcohols dissociate to form alkoxides; aldehydes and ketones form strongly rehybridized η^2(C,O) species on all of the group VIII metal surfaces on which they have been examined. C–H bond activation, including that leading to the proposed formation of oxametallacycles, occurs subsequent to the initial strong metal–oxygen interaction. Relatively few studies have been carried out on surface reactions of adsorbates containing other reactive functions which might compete with carbonyl or hydroxyl groups for surface metal sites. In this work, we consider the adsorption and reaction of the unsaturated C_3 oxygenates, allyl alcohol ($CH_2{=}CHCH_2OH$) and acrolein ($CH_2{=}CHCHO$) in order to probe the competition between olefin and oxygen functions for surface sites and to determine the extent to which this may influence reaction pathways and intermediates relative to those of their aliphatic analogues, 1-propanol and propanal.

The interaction of C=C groups with surfaces of the group VIII metals is quite similar to that of the carbonyl group. Olefins are typically bound in a di-σ configuration (analogous to η^2(C,O) bonding of aldehydes and ketones) at low temperatures, with strong rehybridization of the originally sp^2 carbons resulting in reduction of the C–C stretch frequencies toward those of alkanes.[8] On surfaces with hexagonal symmetry, these typically convert to strongly bound alkylidyne intermediates, such as the ubiquitous ethylidyne, CCH_3.[9-15]

The incorporation of olefinic functions into oxygenates provides the opportunity for multiple coordination of these intermediates to surfaces without requiring prior C–H scission. In effect, these adsorbed molecules should experience increased metal–carbon interactions similar to those of the oxametallacycle intermediates discussed above. The expected consequences of these increased interactions are less clear. For example, we have demonstrated previously that aliphatic alcohols and aldehydes do not decarbonylate via a common pathway on Rh(111);[1,2] only the aldehydes give rise to volatile hydrocarbon products. Increasing interactions with the surface at a point other than the oxygen function might be expected to reduce or to eliminate the divergence of reaction pathways for decarbonylation of, for example, allyl alcohol and acrolein. Similarly, depending on the sequence of C–H and C–C scission reactions, saturated and unsaturated oxygenates may or may not react via common pathways. If they do not, it is unclear how the details of multiple coordination to the surface will alter

---

(1) Houtman, C. J.; Barteau, M. A. *J. Catal.* **1991**, *130*, 528.
(2) Brown, N. F.; Barteau, M. A. *Langmuir*, in press.
(3) Brown, N. F.; Barteau, M. A. In *Selectivity in Catalysis*; Suib, S. L., Davis, M. E., Eds.; ACS Symposium Series, submitted for publication.
(4) Xu, X.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 6779.
(5) Xu, X.; Friend, C. M. *J. Phys. Chem.*, submitted for publication.
(6) Xu, X.; Friend, C. M. *Langmuir*, submitted for publication.
(7) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1266.
(8) Sheppard, N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 589.
(9) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1980**, *117*, 685.
(10) Dubois, L. H.; Castner, D. G.; Somorjai, G. A. *J. Chem. Phys.* **1980**, *72*, 5234.
(11) Gates, J. A.; Kesmodel, L. L. *Surf. Sci.* **1983**, *124*, 68.
(12) Barteau, M. A.; Broughton, J. Q.; Menzel, D. *Appl. Surf. Sci.* **1984**, *19*, 92.
(13) Marinova, Ts. S.; Kostov, K. L. *Surf. Sci.* **1987**, *181*, 573.
(14) Slavin, A. J.; Bent, B. E.; Kao, C.-T.; Somorjai, G. A. *Surf. Sci.* **1988**, *202*, 388.
(15) Yagasaki, E.; Bachman, A. L.; Masel, R. I. *J. Phys. Chem.* **1990**, *94*, 1066.

0002-7863/92/1514-4258$03.00/0

adsorbate stability, i.e., whether surface-bound unsaturated oxygenates will decarbonylate more rapidly or less rapidly than their aliphatic counterparts. Previous studies of the surface chemistry of allyl alcohol and acrolein have been carried out primarily on the group Ib metals,[16,17] where much weaker interactions with the π-systems of adsorbates would be expected to produce less dramatic influences of the olefin function than in the present work on Rh(111).

Experimental Section

The experiments were performed in the two-level stainless steel vacuum chamber described previously.[18,19] Ultrahigh vacuum conditions were achieved through the use of both an ion pump and a diffusion pump to create a base pressure of 2×10^{-10} Torr. The top level was equipped with four-grid optics (Physical Electronics) for LEED and AES experiments, as well as a quadrupole mass spectrometer (UTI 100C) multiplexed with an IBM XT computer for TPD experiments. The lower level contained a HREEL spectrometer (McAllister Technical Services). HREEL spectra were recorded at an electron-beam energy of 5 eV, which produced an elastic peak with a height corresponding to 2×10^5 cps (counts per second) and a fwhm of 70 cm^{-1} when the beam was reflected from a clean Rh(111) surface.

The Rh(111) crystal was polished using standard metallographic techniques and was spot-welded on three 0.5-mm tantalum wires that were used to support as well as to heat the crystal. Heating of the crystal was achieved by passing current (<30 A) through the support wires. A chromel–alumel thermocouple was spot-welded to the back of the crystal in order to monitor the temperature. The crystal could be cooled to 85 K by thermal conduction through a $^1/_4$-in. copper feedthrough, the back side of which was immersed in liquid nitrogen. The Rh(111) crystal was cleaned by cycles of oxygen TPD and annealing to 1350 K. AES, HREELS, and oxygen TPD were used to judge the cleanness of the crystal.

The allyl alcohol and acrolein samples were stored in glass tubes which were attached to a stainless steel dosing line. The samples were purified by repeated freeze–pump–thaw cycles. These reagents were dosed to the crystal through a 1.5-mm stainless steel needle, with the crystal rotated 30° from the needle for exposures from the chamber background.

All TPD spectra have been corrected for mass spectrometer sensitivity using the procedure of Ko et al.[20] Product identification and quantification required deconvolution of the contributions of the fragments of the various products to each of the *m/e* channels monitored. Experimentally determined fragmentation patterns were utilized in this analysis, as previously described.[1,19] No correction for ionization gauge sensitivity was made when determining exposure of reactant. From LEED measurements it was determined that a CO exposure of 0.6 langmuir (1 langmuir = 10^{-6} Torr s) resulted in a 0.33-monolayer (ML) coverage on Rh(111). One monolayer is defined as the number of surface Rh atoms on the (111) surface, 1.62×10^{15} atoms/cm^2. The area obtained by integration of the CO desorption spectrum after a CO exposure of 0.6 langmuir was then used to convert TPD peak areas to the absolute yields of desorbing products.

Results

Temperature Programmed Desorption Experiments. Allyl alcohol decomposed unselectively on the clean Rh(111) surface, liberating CO and H_2, but no volatile hydrocarbon products. In contrast, acrolein produced ethane and ethylene, as well as CO and hydrogen. Complete TPD spectra for allyl alcohol and acrolein at saturation coverages on Rh(111) are illustrated in Figures 1 and 2, respectively. This behavior is directly analogous to that observed for decarbonylation of aliphatic C_2 and C_3 oxygenates on this surface. Acetaldehyde decomposed to CH_4, CO, and H_2; propanal released C_2H_6, CO, and H_2; but *no* hydrocarbon products desorbed in TPD experiments with either ethanol or 1-propanol on Rh(111).[1,2]

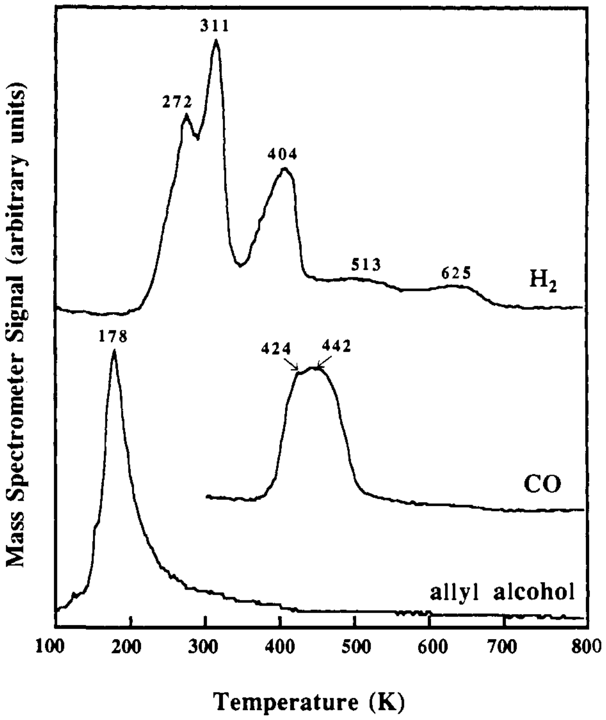


Figure 1. TPD spectra following a saturation exposure of 2.9 langmuirs of allyl alcohol on the clean Rh(111) surface at 91 K.

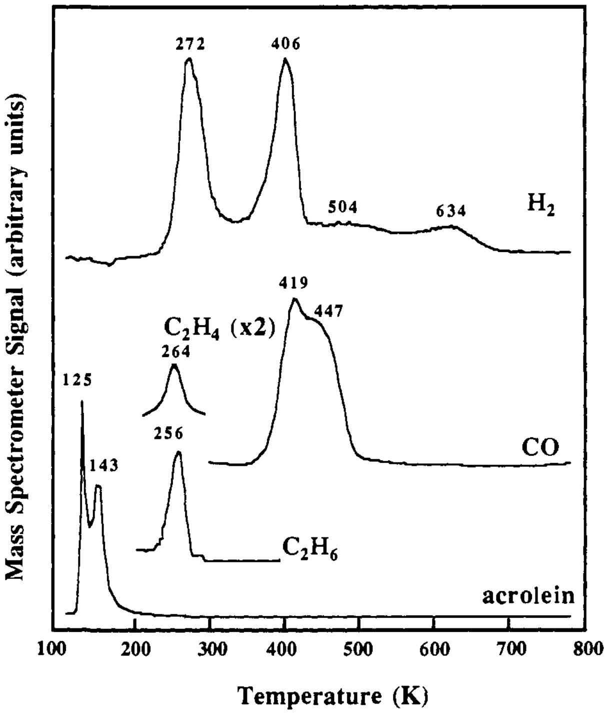


Figure 2. TPD spectra after exposure of 2.7 langmuirs of acrolein on the clean Rh(111) surface at 91 K.

Other than the absence of C_2 hydrocarbons from allyl alcohol, the TPD spectra for allyl alcohol and acrolein on Rh(111) are remarkably similar. Both give rise to broad, overlapping peaks for CO desorption at ca. 420–450 K and a prominent peak for H_2 at 405 K, with smaller shoulders at ca. 510 and 630 K. These three H_2 peaks are consistent with the sequential dehydrogenation of surface ethylidyne species, and quite similar H_2 peaks above ca. 400 K have been observed previously for decomposition of ethylidynes produced by adsorption of ethylene[21] or propanal[2] on this surface. Likewise, the envelope of CO peaks at 420–450 K is both broader and at lower temperature than that for CO from a clean Rh(111) surface (which typically desorbs at 470–490 K) and has been shown previously to be characteristic of CO desorption from a coadsorbed CO and ethylidyne layer.[22] The

---

[16] Brainard, R. L.; Peterson, C. G.; Madix, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4553.

[17] Solomon, J. L.; Madix, N. J. *J. Phys. Chem.* **1987**, *91*, 6241.

[18] Davis, J. L.; Barteau, M. A. *Surf. Sci.* **1989**, *208*, 383.

[19] Houtman, C.; Barteau, M. A. *J. Phys. Chem.* **1991**, *95*, 3755.

[20] Ko, E. I.; Benziger, J. B.; Madix, R. J. *J. Catal.* **1980**, *62*, 264.

[21] Bent, B. E.; Mate, C. M.; Crowell, J. E.; Koel, B. E.; Somorjai, G. A. *J. Phys. Chem.* **1987**, *91*, 1493.

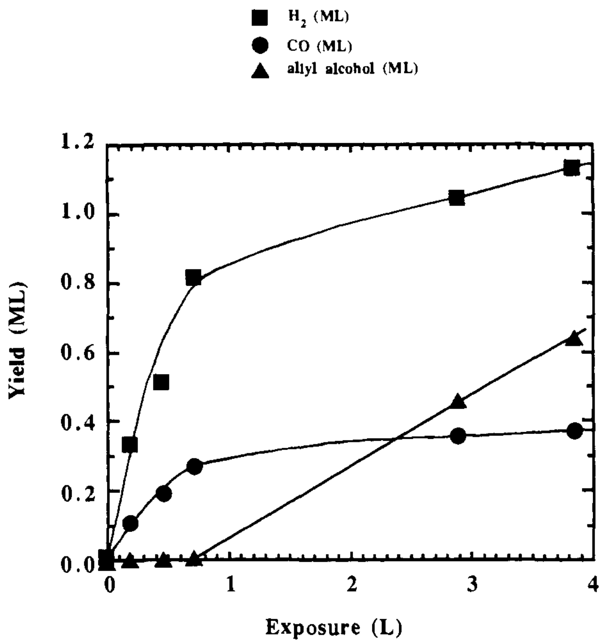


Figure 3. TPD yields versus allyl alcohol exposures on the clean Rh(111) surface. The vertical axis has units of monolayers of molecules. A monolayer (ML) is defined as the number of Rh atoms in the top layer of the close-packed surface, 1.62×10^{15} atoms/cm^2. The horizonal axis has units of langmuirs uncorrected for ionization gauge sensitivity.

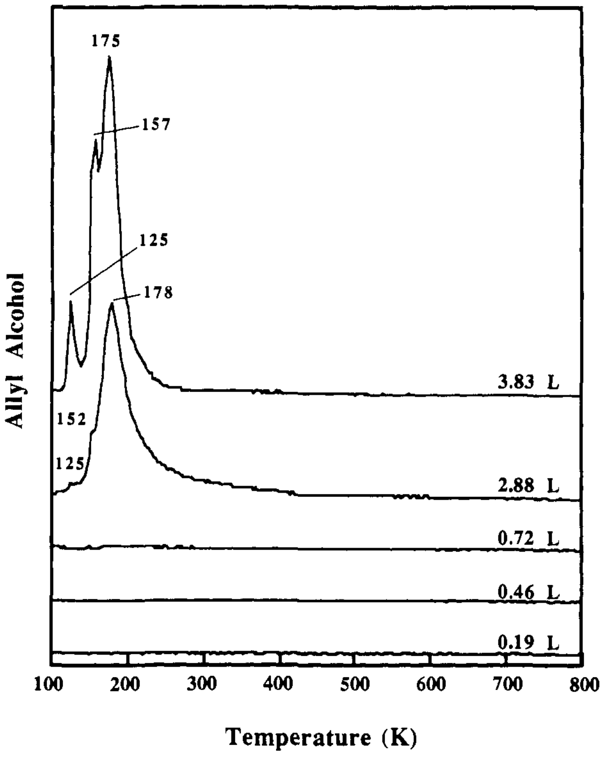


Figure 4. Desorption of allyl alcohol from the Rh(111) surface after the indicated exposures at ca. 90 K.

characterization of the TPD spectra for both acrolein and allyl alcohol above 325 K as due to coadsorbed ethylidyne and CO was confirmed by HREEL spectra of the respective adlayers, as described below.

The routes to this common adlayer from acrolein and allyl alcohol differ, as might be expected, from the divergence of reaction pathways for their aliphatic analogues,[1,2] and some of these differences are reflected in the portions of the TPD spectra below ca. 350 K in Figures 1 and 2. While both reactants give rise to a desorption peak for H_2 at 272 K characteristic of desorption-limited evolution of H_2,[23] and both give rise to a variety of desorption states for the parent molecule below 200 K, only allyl alcohol leads to H_2 at 311 K, and only acrolein produces ethane and ethylene at ca. 260 K.

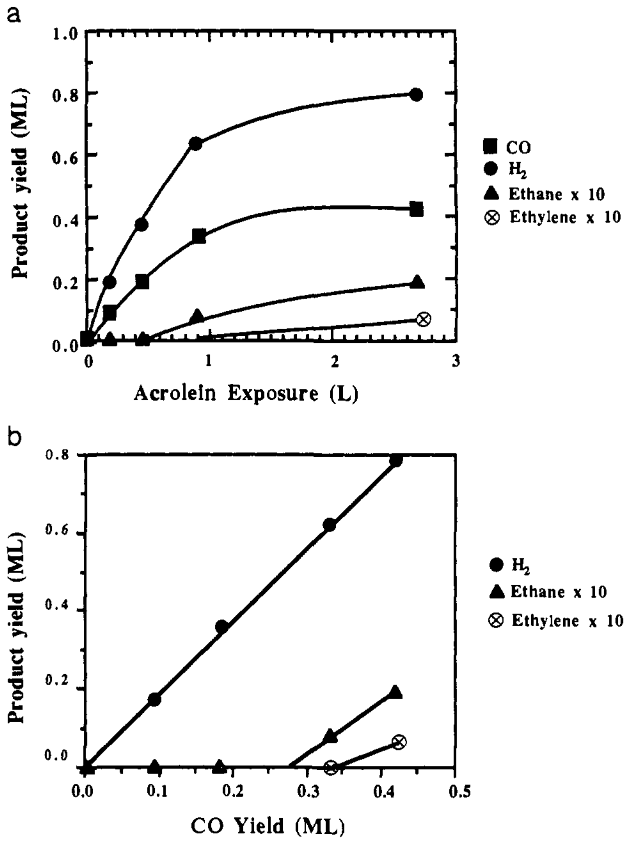


Figure 5. (a) TPD yields after acrolein exposure on the clean Rh(111) surface plotted versus exposure of acrolein. The vertical axis has units of monolayers of molecules. A monolayer (ML) is defined as the number of Rh atoms in the top layer of the close-packed surface, 1.62×10^{15} atoms/cm^2. The horizonal axis has units of langmuirs uncorrected for ionization gauge sensitivity. (b) TPD yields after acrolein exposures versus the yield of CO. Both the vertical axis and the horizonal axis have units of monolayers of molecules.

The data illustrated in Figures 1 and 2 were obtained for alcohol or aldehyde exposures of ca. 2.8 langmuirs, sufficient to saturate the various decomposition channels for these two molecules. Some variations were observed at lower exposures, but the distinctions between allyl alcohol and acrolein noted above were generally preserved. For example, Figure 3 illustrates the variation of yields for CO, H_2, and allyl alcohol following adsorption of allyl alcohol below 100 K. For exposures below about 0.7 langmuir, all adsorbed alcohol molecules decomposed, and CO and H_2 were the only species desorbed. These were produced in the 1:3 ratio expected from the stoichiometry of the reactant. For exposures between ca. 1 and 3 langmuirs, the decomposition channels saturated, and the various desorption peaks for the reactant were populated. The sequential filling of these states is illustrated in greater detail in Figure 4. Three peaks were observed for allyl alcohol desorption, at 175, 157, and 125 K. These were populated sequentially, with the two at higher temperatures saturating at exposures below ca. 3 langmuirs. The magnitude of the 125 K peak increased indefinitely with further exposure, characteristic of desorption from condensed multilayers.

Desorption of acrolein also occurred from a multilayer state at 125 K and a monolayer state at 143 K, both of which are evident in Figure 2. Unlike allyl alcohol (but like the corresponding

---

[22] Blackman, G. S.; Kao, C. T.; Bent, B. E.; Mate, C. M.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1988**, *207*, 66.

[23] Yates, J. T., Jr.; Thiel, P. A.; Weinberg, W. H. *Surf. Sci.* **1979**, *84*, 427.

Table I. Allyl Alcohol HREELS Assignments

mode	IR[a]	adsorbed on Pd(111)[b]	adsorbed on Rh(111)
ν(OH)	3400	3380	3365
$\nu_a(CH_2)$	3092	3135	3110
$\nu(CH_2)$	2923	2950	2885
ν(CC)	1603	1610	1675
$\delta(CH_2)$, δ(CH)	1371-1457	1390	1450
δ(OH)	1324	nr[c]	nr
$\rho(CH_2)$	1190	1200	nr
ν_a(CCO)	1103	1000	1020
$\rho(CH_2)$	962	1000	1020
ν_s(CCO)	910, 885	905	945
γ(CH)	nr	815	750
δ(CCC)	608, 442	515	560
δ(CCO)	344	350	355

[a] Reference 24. [b] Reference 25. [c] Not resolved = nr.

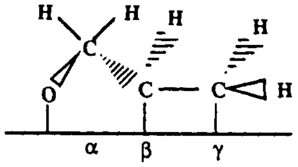
aliphatic aldehydes), the decomposition selectivity for acrolein was coverage-dependent. As shown in Figure 5, CO and H_2 were the only volatile decomposition products for acrolein exposures below ca. 0.5 langmuir. At higher exposures, formation of ethane and ethylene was also observed. This threshold behavior for production of volatile hydrocarbons by aldehyde decarbonylation was previously observed for methane from acetaldehyde[1] and ethane from propanal[2] and is most clearly illustrated by plotting hydrocarbon yield vs CO yield as in the lower portion of Figure 5. The origin of this phenomenon is not completely clear. Houtman[1] previously demonstrated that the threshold coverage for methane production from acetaldehyde could be reduced by coadsorption of hydrogen; however, the absence of volatile hydrocarbon production from the more hydrogen-rich alcohols argues against hydrocarbon production being limited solely by hydrogen availability. It is likely that CO produced by aldehyde decarbonylation inhibits the decomposition of the hydrocarbon moiety produced by this reaction, and that a critical level of CO is required to poison the surface in this fashion. The exact coverage of CO required appears to depend on the aldehyde reactant: methane is observed from acetaldehyde for CO yields above 0.05 ML, ethane from propanal for $\theta_{CO} > 0.15$ ML, and ethane and ethylene from acrolein for $\theta_{CO} > 0.25$ ML. Clearly the hydrocarbon yield is influenced by a number of factors, including the identity of the hydrocarbon ligand eliminated, its hydrogen deficiency, the availability of hydrogen atoms on the surface, and the coverage of inhibitors such as CO. Again, while all of these come into play for hydrocarbon evolution from aldehydes, we have observed *no* volatile hydrocarbon formation from any primary alcohol on Rh(111), clearly reflecting fundamental differences in the interactions of these two types of oxygenates with this surface.

High-Resolution Electron Energy Loss Spectroscopy. Insights into the details of the surface–adsorbate interaction and into the identities of adsorbed reaction intermediates can often be provided by vibrational spectroscopy. HREEL spectra for an adsorbed layer of allyl alcohol and the adlayers derived by heating it are illustrated in Figure 6. Allyl alcohol adsorbs molecularly on the Rh(111) surface at 91 K, as is evident from its nearly unperturbed (relative to the liquid state[24]) vibrational spectrum at 91 K. On Rh(111) the O–H stretch was observed at 3365 cm^{-1}, the ν(CCO) stretch at 1020 cm^{-1}, and the ν(C=C) stretch at 1675 cm^{-1}. The origin of the slight blue-shift of the ν(C=C) mode on Rh(111) is unclear. Losses characteristic of CH_2 bending modes were also evident. The frequencies characteristic of allyl alcohol in the liquid phase[24], on Pd(111),[25] and on Rh(111) are summarized in Table I. Heating the crystal to 207 K resulted in the elimination of the ν(OH) mode and the ν(C=C) mode. Modes characteristic of ν(CCO) and the CH_2 bending modes remained.

Disappearance of the ν(OH) vibration is suggestive of dissociation of the O–H bond to form adsorbed alkoxides and hydrogen atoms on the surface and has been observed to occur in this temperature range for other alcohols on Rh(111).[1,2,26] The hydrogen atoms produced by this step recombine and desorb at 270 K with kinetics characteristic of H-atom recombination; the alkoxide moieties ultimately decarbonylate.

The disappearance of the ν(C=C) mode for allyl alcohol between ca. 100 and 200 K suggests that the adsorbed species produced cannot be described simply as an oxygen-bound alkoxide. Similar disappearances of the stretching modes characteristic of double bonds occur for C=O groups of aldehydes and ketones, and for C=C groups of olefins, and are characteristic of rehybridization to more nearly sp^3 centers. Bent et al.[27] have shown, for example, that reduction of the CC bond order for ethylene to ca. 1.2–1.5 reduces the ν(C=C) frequency to ca. 1480 cm^{-1} on rhodium surfaces. A comparable shift of the ν(C=C) mode of adsorbed allyl alcohol or alkoxide species would place this loss squarely beneath the intense C–H bending modes, effectively obscuring it.

The disappearance of both the ν(OH) and ν(CC) modes for allyl alcohol below 200 K suggests that the allyl alkoxide is coordinated to the surface at both its oxygen and olefin functions. While such coordination to a single metal center would require the allyl alkoxide ligand to be significantly strained, on an extended metal surface it is possible to form a relatively unstrained species.



As can be seen from this diagram, the β and γ carbons are coordinated to the surface in this structure, but the α carbon is separated from the surface by the alkoxide oxygen.

Decarbonylation of this η^3-allyl alkoxide intermediate occurred upon further heating of the sample. Losses corresponding to the ν(CO) modes of linear (2025 cm^{-1}) and bridge-bonded (1785 cm^{-1}) molecular CO are evident in the HREEL spectrum obtained after heating to 278 K in Figure 6. Further heating to 304 K was sufficient to complete the decarbonylation reaction; the spectrum obtained at this temperature is considerably less complex than that at 278 K and can be clearly assigned to adsorbed ethylidyne and CO species. The modes characteristic of ethylidynes are the $\rho(CH_3)$ at 980 cm^{-1}, the ν(CC) at 1135 cm^{-1}, the prominent $\delta(CH_3)$ at 1370 cm^{-1}, and the $\nu(CH_3)$ at 2985 cm^{-1}. These are in excellent agreement with respect to both position and relative intensity with spectra obtained for ethylidynes derived from ethylene[10] and propanal[2] on the Rh(111) surface. Some signs of ethylidyne formation from the onset of decarbonylation can be found in the 278 K spectrum of Figure 6, particularly in the growth of the $\delta(CH_3)$ mode at 1360 cm^{-1}. However, the adlayer formed by heating adsorbed allyl alcohol to 278 K is clearly a complex mixture of η^3-allyl alkoxide, ethylidyne, and linear and bridging CO species, as well as possibly other decomposition fragments, and the corresponding HREEL spectrum is difficult to assign in detail.

The net decarbonylation of allyl alkoxides to ethylidynes plus CO would be expected to liberate two hydrogen atoms on the basis of the stoichiometry of these species. This is a plausible source for the H_2 peak observed at 311 K in the TPD spectrum for allyl alcohol decomposition in Figure 1. This peak cannot be separated completely from the recombination-limited H_2 peak at 272 K, but the relative magnitudes of the two are consistent with the 1:2 ratio expected for the initial loss of the hydroxyl hydrogen, followed by loss of two hydrogens accompanying the decarbonylation reaction. Likewise, although one might, in principle, extract the kinetics of the decarbonylation reaction from the 311 K H_2 peak, we have previously shown that the kinetics of H_2 evolution from organic adsorbates on Rh(111) in this temperature range is in-

---

(24) Silvi, B.; Perchard, J. P. *Spectrochim. Acta* **1976**, *32A*, 11.
(25) Davis, J. L.; Barteau, M. A. *J. Mol. Catal.*, submitted for publication.
(26) Houtman, C.; Barteau, M. A. *Langmuir* **1990**, *6*, 1558.
(27) Bent, B. E.; Mate, C. M.; Kao, C.-T.; Slavin, A. J.; Somorjai, G. A. *J. Phys. Chem.* **1988**, *92*, 4720.
(28) Oelichmann, H. J.; Bougeard, D.; Schrader, B. *J. Mol. Struct.* **1981**, *77*, 149.

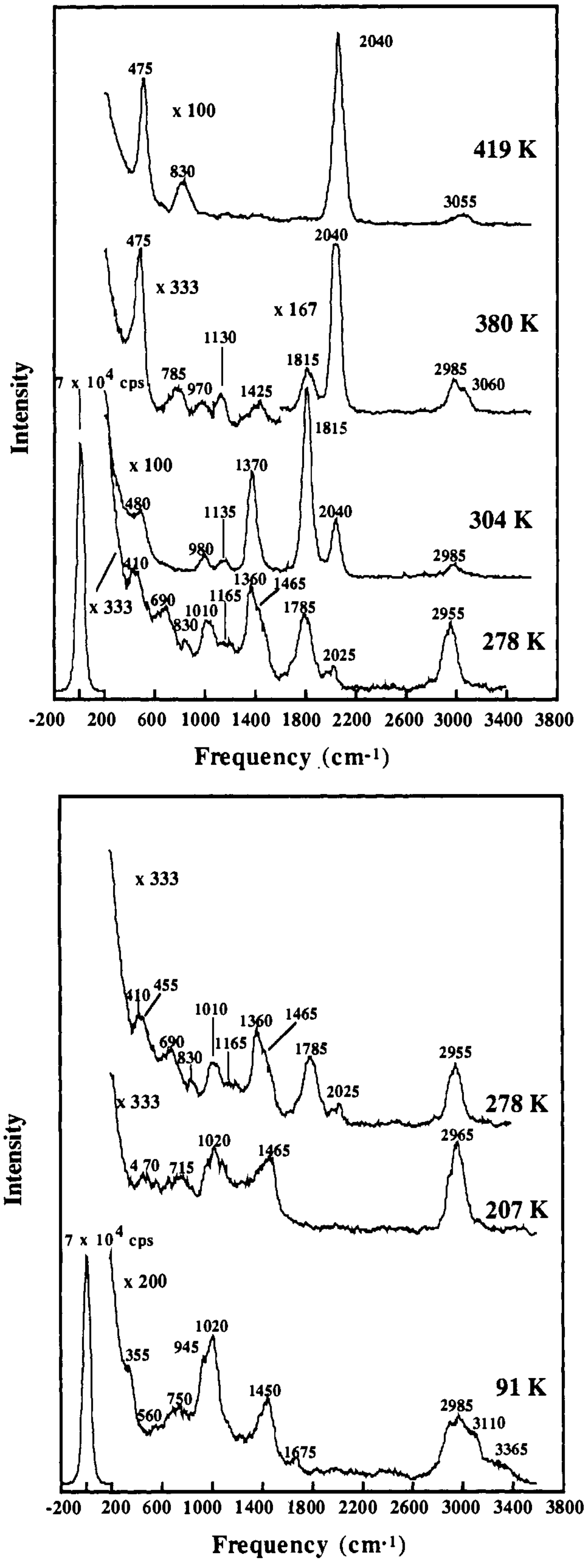


Figure 6. HREEL spectra after an exposure of 1.3 langmuirs of allyl alcohol on the clean Rh(111) surface at 91 K and after subsequent heating to the temperatures indicated.

fluenced by both C–H scission and H-atom recombination processes.[19]

The assignment of the spectrum for the allyl alcohol-derived adlayer at 304 K to coadsorbed ethylidyne and CO species is quite consistent with the TPD results, as noted above. Ethylidynes on Rh(111) typically dehydrogenate to acetylides (CCH), giving rise to the large H_2 desorption peak at 405 K.[2] Subsequent dehydrogenation of the acetylide produces the H_2 peaks at 510 and 630 K and deposits carbon atoms on the surface. This species can be tracked by HREELS as well. Between 304 and 419 K in Figure 6, the ethylidyne modes disappear, those for acetylides (830 and 3055 cm^{-1}) appear, and all adsorbed CO is converted to the linear form with ν(CO) at 2040 cm^{-1}. The ability of ethylidynes to force CO into less favorable sites, and the restoration of CO to the preferred linear configuration upon ethylidyne removal, have previously been demonstrated for coadsorbed CO and ethylidyne adlayers on Rh(111) and (100) surfaces.[14,22]

Table II. Acrolein HREELS Assignments

mode	IR[a]	adsorbed on Rh(111)
$\nu_a(CH_2)$	3100	3100
$\nu_s(CH_2)$	3000	3100
ν(CH)	3000	3100
ν(CH)	2800	3100
ν(C=O)	1724	1410
ν(C=C)	1625	1645
$\delta(CH_2)$	1420	1410
ρ(CH)	1275	nr[b]
ν(CC), $\rho(CH_2)$	1158	1170
$\rho(CH_2)$, ν(CC)	912	1010
δ(CCO)		605

[a] Reference 28. [b] Not resolved = nr.

Like allyl alcohol, acrolein shows evidence of multiple coordination to the surface, and a portion of the adsorbed molecules decarbonylate to deposit CO and ethylidynes on the surface. However, the details of the interactions of these two molecules with the surface appear to differ, as do the routes by which they decarbonylate.

Acrolein and other aldehydes adsorb on the Rh(111) surface at 91 K in an η^2(C,O) configuration, i.e., the carbonyl group is rehybridized by interaction with the surface. The η^2(C,O) state is the preferred binding configuration for aliphatic aldehydes and ketones on group VIII metal surfaces and is characterized by a strong decrease in the carbonyl stretching frequency from that in the gas or liquid phase, with relatively little perturbation of pendant alkyl groups. On Rh(111) we have observed previously that the ν(C=O) frequencies of carbonyl compounds shift from above 1700 cm^{-1} for condensed layers to 1380, 1450, and 1460 cm^{-1} for η^2(C,O)-bound acetone, acetaldehyde, and propanal, respectively. The 91 K HREEL spectrum of adsorbed acrolein in Figure 7 is consistent with assignment to an η^2(C,O) species and, like the low-temperature spectra of the aliphatic aldehydes, also shows a small peak for the unperturbed ν(C=O) mode of condensed species at 1720 cm^{-1}. The shift of the ν(C=O) frequency from 1720 cm^{-1} for the unperturbed molecule to ca. 1400 cm^{-1} for η^2(C,O) species places this loss beneath the CH_2 bending mode at 1410 cm^{-1}. The breadth of the peak at 1410 cm^{-1} relative to most others in Figures 5 and 6 supports the assignment of the envelope at 1410 cm^{-1} to both the ν(C=O) and $\delta(CH_2)$ modes. The remaining frequencies associated with the vinyl group are essentially unperturbed (Table II); the ν(C=C) stretch remains at roughly its gas-phase frequency. Supporting evidence for this binding configuration, in particular for the absence of rehybridization of the C=C group, comes from the ν(C–H) frequency of 3100 cm^{-1}. This frequency is characteristic of hydrogen bound to sp^2 carbon centers and is well above that for sp^3-hybridized hydrocarbons.

Slight heating of the surface, to 147 K, was sufficient to desorb molecular acrolein as shown in Figure 2 and to leave more strongly bound (and strongly rehybridized) species on the surface. Between 91 and 147 K the HREEL spectrum changed dramatically. The ν(C=C) mode at 1645 cm^{-1} disappeared, and the ν(C–H) frequency decreased to ca. 3000 cm^{-1}, characteristic of sp^3-hybridized centers. The δ(CCO) loss at 605 cm^{-1}, characteristic of the bending of the vinyl group with respect to the carbonyl axis, also disappeared, suggesting that both the C=O and C=C groups of the adsorbed acrolein had become anchored to the surface. The remaining modes showed relatively small frequency shifts, but

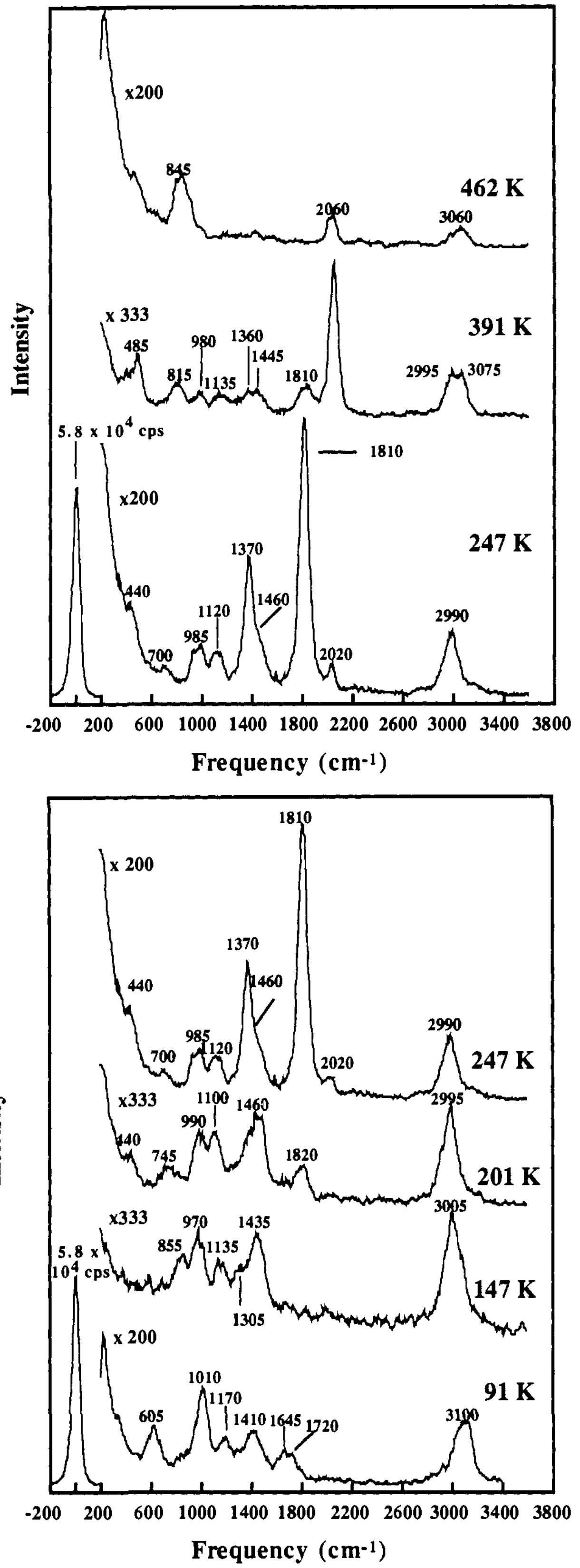


Figure 7. HREEL spectra after an exposure of 2.6 langmuirs of acrolein on the clean Rh(111) surface at 91 K and after subsequent annealing to the indicated temperatures.

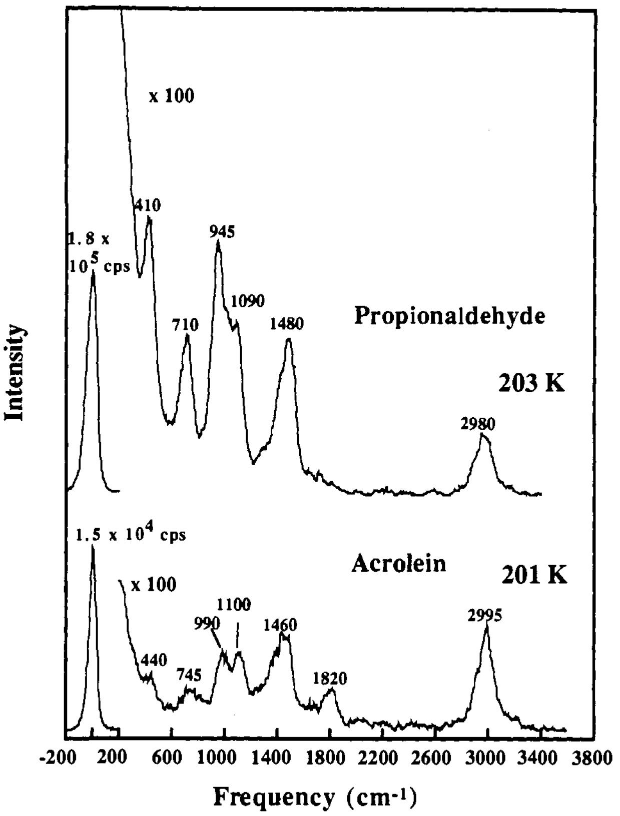


Figure 8. Comparison of the spectrum obtained after exposure to 2.6 langmuirs of acrolein and annealing to 201 K with that obtained after exposure of 2.16 langmuirs of propanal, annealed to 203 K.

considerable changes in their relative intensities, again consistent with a change in the orientation of the CCCO framework with respect to the surface. In accord with its interaction with the surface at all points along its skeleton, acrolein underwent decarbonylation on the Rh(111) surface at lower temperature than did any aliphatic higher alcohol, aldehyde, or ketone. Evidence for the onset of decarbonylation is present in the form of a loss at 1820 cm^{-1} for bridge-bonded CO in the 201 K spectrum of Figure 7. This reaction was essentially complete by 247 K; the corresponding spectrum shows the unmistakable fingerprints of ethylidyne and bridging CO species, with traces of linearly bound CO at 2020 cm^{-1}. The fate of these is essentially the same as that of coadsorbed ethylidyne plus CO layers derived from propanal or from allyl alcohol. The ethylidynes decompose to acetylides, liberating hydrogen at ca. 400 K; CO shifts from the bridge to the linear state as the ethylidynes are removed. From TPD experiments this CO desorbs below 450 K, and the acetylides dehydrogenate at 500–600 K. This behavior is also characteristic of the higher temperature spectra in Figure 7; the ethylidyne modes are suppressed by heating to 391 K, and the principal C=O loss shifts to 2060 cm^{-1}. Most of the CO desorbs upon heating to 462 K, and the characteristic fingerprints of acetylides, losses at ca. 840 and 3050 cm^{-1}, are apparent in this spectrum.

Discussion

The interactions of allyl alcohol and acrolein with the Rh(111) surface may be summarized as follows. Although both molecules give rise to strong interactions of their C=C groups with the surface prior to decarbonylation, much of their chemistry is analogous to that of their aliphatic counterparts. Both interact initially via their oxygen atoms; allyl alcohol dissociates to form its alkoxide, and acrolein binds in an η^2(C,O) configuration, like their aliphatic analogues. Both decarbonylate, but only the aldehydes give rise to volatile hydrocarbons; there is no evidence for formation of adsorbed aldehydes from any alcohol, saturated or unsaturated, on Rh(111). Beyond these important similarities, however, the consequences of strong interactions of the olefinic functions in these molecules with the metal surface are much less predictable. For example, decarbonylation of acrolein occurs at a *lower* temperature than that of propanal, but that of allyl alcohol occurs at a *higher* temperature than that of 1-propanol, as demonstrated by the HREEL spectra of these four molecules in Figures 8 and 9. By 201 K, molecular CO is evident in the spectrum of the adsorbed acrolein layer, but no CO is released from pro-

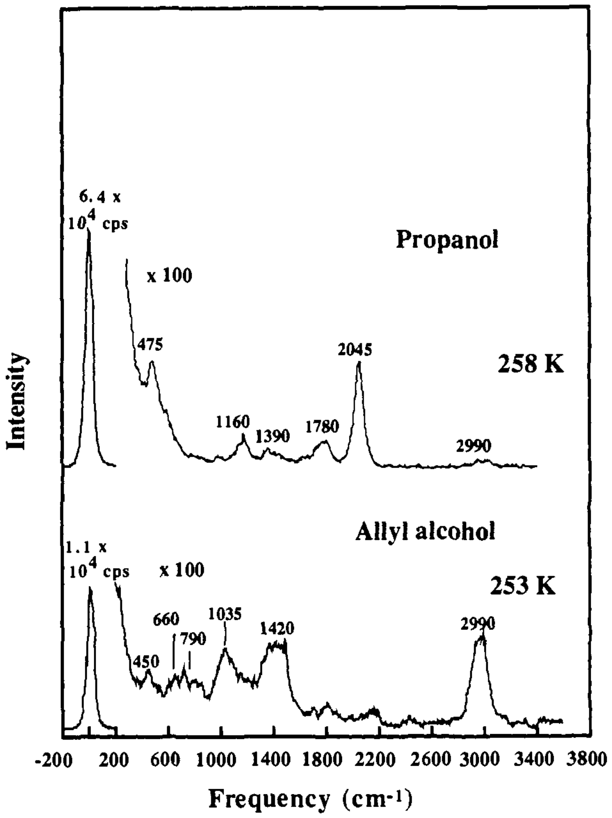


Figure 9. Comparison of the spectrum obtained after exposure of 1.3 langmuirs of allyl alcohol and annealing to 253 K with that obtained after exposure of 4.2 langmuirs of propanol, annealed to 258 K.

pionaldehyde at this temperature. The decarbonylation of acrolein is complete by 250 K, whereas that of propanal continues to 300 K. In contrast, the onset of CO release from 1-propanol is essentially complete by 250 K, whereas no CO is present in the spectrum of allyl alcohol at this temperature. Thus, the interaction of the C=C function with the surface destabilizes the aldehyde but stabilizes the alkoxide relative to the saturated analogues.

This apparent anomaly and others, e.g., formation of ethylidynes from allyl alcohol but not 1-propanol, suggest that the details of the decarbonylation reactions of higher oxygenates are crucial. For example, although decarbonylation of both allyl alcohol and acrolein produces ethylidynes plus CO, it is unlikely that a common intermediate is responsible in both cases; it is unclear whether the same hydrocarbon ligand is eliminated in both cases or, indeed, that this ligand in either case is the ethylidyne ultimately isolated. However, the divergence of reaction pathways for alcohols and aldehydes and the differences in the chemistry of saturated vs unsaturated oxygenates allow the field of candidate hydrocarbon ligands to be narrowed considerably. The logic behind this process is described below.

Previous studies have suggested that aldehyde decarbonylation on Rh(111) involves an initial scission of an α C–H bond to form an adsorbed acyl.[1] In contrast, ketones do not decompose via acyls, since acyl formation would require C–C rather than C–H scission. While stable acyls have not been isolated on Rh(111) for spectroscopic examination, they have been detected in HREELS studies on Pd(111).[29] Our studies of aliphatic aldehydes suggest that aliphatic acyls undergo C–C scission to release CO and an alkyl ligand one carbon shorter than the parent aldehyde. Evidence for direct C–C scission includes (1) the absence of a kinetic isotope effect for decarbonylation of CD_3CDO vs CH_3CHO on Rh(111)[1] and (2) the clean formation of CH_3D by decarbonylation of acetaldehyde in the presence of coadsorbed deuterium atoms.[1]

If one extends this analogy to the unsaturated aldehyde, acrolein, C–C scission of the corresponding acyl intermediate (propenoyl, $CH_2CHC{=}O$) would release a vinyl ($CH_2{=}CH$) ligand to the surface. While this must be considered the leading candidate, it is by no means the only one possible. Other conceivable leaving groups include those with a greater number of hydrogens (e.g., C_2H_5, CH_3CH, or CH_2CH_2), isomers of the vinyl ligand (e.g., CH_3C), and those with fewer hydrogens (e.g., CH_2C or $HC{\equiv}CH$). Although hydrogen is available (from prior α C–H scission) to form $C_2H_{n\geq 4}$ ligands by hydrogenation of the propenoyl before C–C scission, this appears to be unlikely on several grounds. First, there is no evidence for the products of such reactions either in the HREEL spectra or in the TPD spectra, where one might expect to find the saturated products of autohydrogenation of unsaturated aldehydes and alcohols. Second, it is difficult to envision hydrogenation of the vinyl group of acrolein while preserving the divergence of reaction kinetics, pathways, and products between this reactant and other C_3 oxygenates such as propanal.

Likewise, isomerization of the propenoyl intermediate and direct elimination of an ethylidyne moiety is also unlikely, at least as a route to production of ethylene and ethane from acrolein. Ethylidynes are generally "dead ends" on transition metal surfaces and appear to be side products rather than intermediates in reactions such as ethylene hydrogenation.[30,31] We have also shown that, in the case of propanal decarbonylation, gas-phase ethane and adsorbed ethylidynes are formed by parallel rather than sequential reactions.[2] Likewise, as CH_2C must be a transient intermediate in the dehydrogenation of ethylidynes, CH_3C, to acetylides, HCC, a reaction which does not lead to volatile hydrocarbons, this intermediate is also an unlikely product of the elementary decarbonylation step.

Thus vinyl, $CH_2{=}CH$, and acetylene, $CH{\equiv}CH$, are the most likely candidates for ligands eliminated in acrolein decarbonylation. Vinyl elimination would make acrolein decarbonylation directly analogous to that of the aliphatic aldehydes, for which alkyl elimination is more firmly established. However, if this is the case, one must ask why, if the same ligand is produced by allyl alcohol decomposition, no volatile C_2 hydrocarbon products are observed from the alcohol. Acetylene could be produced by either sequential or concerted scission of the γ C–H and α C–C bonds of the propenoyl. It can be connected to more highly hydrogenated C_2 products; acetylene adsorbed on Rh(111) undergoes hydrogenation to ethylene and ethylidyne species.[10]

One can follow a similar deductive process for decarbonylation of allyl alcohol. HREELS spectra of this adsorbate and of its saturated counterparts firmly establish that alcohols form stable alkoxides on Rh(111) at quite low temperatures. Studies of the aliphatic alkoxides and of epoxides suggest that the next step is scission of a β C–H bond to form an oxametallacycle. For allyl alcohol, this C–H scission would be unnecessary: the β and γ carbons are already hydrogen-deficient, and HREELS shows clear evidence for strong interactions between the C=C group and the surface. The $\eta^3(C_\gamma,C_\beta,O)$ oxametallacycle for the allyl alkoxide should be a highly strained intermediate (though this may be lessened by coordination to several surface Rh atoms), and α C–C scission to produce decarbonylation is the logical next step. If this is the case, the ligand eliminated will again be a vinyl species. Whatever its identity, it yields adsorbed ethylidynes but no volatile hydrocarbon products; in this regard, decarbonylation of allyl alcohol resembles that of neither acrolein nor 1-propanol. Since the temperatures for decarbonylation of the propenoyl from acrolein and of the allyl alkoxide from allyl alcohol differ by ca. 70 K, it is conceivable that a vinyl ligand is eliminated in both cases, but that the selectivity of its subsequent reaction to volatile products vs ethylidynes depends upon the kinetics of these competing reactions. By altering the temperature at which the vinyl ligand is liberated, one can affect the selectivity of its subsequent reaction. If ethylidyne formation is the more highly activated process, the yield of volatile hydrocarbons would decrease for decarbonylations occurring at higher temperatures (e.g., that of

---

(29) Davis, J. L.; Barteau, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 1782.

(30) Beebe, T. P., Jr.; Albert, M. R.; Yates, J. T., Jr. *J. Catal.* **1985**, *96*, 1.

(31) Zaera, F. *J. Phys. Chem.* **1990**, *94*, 5090.

allyl alcohol vs that of acrolein). Alternatively, one could argue that acrolein liberates vinyl groups and allyl alcohol liberates acetylene; the former would then lead to ethylidynes, ethylene, and ethane, but the latter to ethylidynes only. Candidates for elimination from saturated C_3 oxygenates include ethyl from propanal, and ethylidene (CH_3CH) or vinylidene ($CH_2{=}C$) from 1-propanol and propylene oxide.

A final note concerns the identity of the carbonyl-containing ligands liberated by C–C scission. If aldehydes decarbonylate via acyls, subsequent C–C scission in these will release CO directly. On the other hand, if the alcohols form strained oxametallacycle intermediates, it is difficult to imagine that complete dehydrogenation of the α carbon will precede ring-opening. Ring-opening prior to a C–H scission would release formaldehyde (H_2CO) or formyl (HCO) intermediates. Unfortunately these are quite difficult to detect under the conditions of these experiments; formyls have not been convincingly isolated on any single crystal transition metal surface, and formaldehyde dehydrogenates on Rh(111) at quite low temperatures (ca. 130 K[26,32]), well below those of higher alcohol decomposition. If such species are indeed intermediates in higher alcohol decarbonylation, microscopic reversibility would suggest that higher alcohols might be synthesized by, for example, formyl addition to surface hydrocarbon ligands, rather than by the CO insertion step typically invoked by analogy with mechanism of homogeneous hydroformylation.

Conclusions

The principal influences of the C=C group of allyl alcohol and acrolein are on the bonding configuration of these molecules on the Rh(111) surface and on the stability of the corresponding intermediates. Acrolein is adsorbed in an η^4(C,C,C,O) configuration and decarbonylates at lower temperatures than does its aliphatic analogue, propanal. Allyl alcohol dissociates to form allyl alkoxides which are bound in an η^3(C,C,O) configuration; these decarbonylate at higher temperatures than does *n*-propoxide. The decarbonylation selectivities of these reactants mirror those of their aliphatic counterparts, again demonstrating the divergence of the reaction pathways for alcohols and aldehydes. Acrolein, like the aliphatic aldehydes, gives rise to volatile hydrocarbon products one carbon shorter than the parent; neither allyl alcohol nor any primary alcohol produces volatile hydrocarbons on Rh(111). These results suggest that the hydrocarbon ligands and carbonyl moieties released by decarbonylation of aldehydes and alcohols on Rh(111) may differ, and that the corresponding synthesis of higher oxygenates may be similarly complex.

Acknowledgment. We gratefully acknowledge the support of this research by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences (Grant FG02-84ER13290). We also thank Professor C. M. Friend for providing copies of refs 4–6 prior to publication.

Registry No. $CH_2{=}CHCHO$, 107-02-8; $CH_2{=}CHCH_2OH$, 107-18-6; Rh, 7440-16-6.

---

(32) Houtman, C.; Barteau, M. A. *Surf. Sci.* 1991, *248*, 57.

Dynamics of the Reaction $CH_2OH^+ \rightarrow CHO^+ + H_2$. Translational Energy Release from ab Initio Trajectory Calculations

Einar Uggerud* and Trygve Helgaker

Contribution from the Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway. Received September 25, 1991

Abstract: The classical equations of motion have been solved for the title reaction on the route leading from transition state to separated products using ab initio potential energy functions (HF and CASSCF). The calculations reproduce the experimentally observed translational energy release for both wave functions. Isotope effects on the translational energy release are also in good agreement with experiment. The calculations reveal that the translational energy release is a complicated function of the motion along the whole reaction trajectory. The situation at the transition state is not sufficient for predicting the final energy distribution.

I. Introduction

An important characteristic of unimolecular decompositions is the energy released as relative motion between the fragments.[1] When the reaction has a large barrier to the reverse reaction, the dominating source of the relative translational energy is the potential energy difference between the transition state and the separated products. The relative amount of this energy that ends up as translation is determined by the dynamics of the reaction. Therefore, the relative translational energy release[2] is a sensitive probe of the energy surface in the exit valley of the reaction. Of particular interest is the variation of the translational energy with isotopic substitution.

Large double focussing mass spectrometers are ideal for high-resolution measurements of translational energy release[3] upon fragmentation of ions. A large number of measurements have been carried out, but few investigators have been able to give their experimental observations the treatment needed for a precise analysis of the reaction studied.[4] The most successful approach so far originates from Derrick and co-workers (vide infra).

Recently, we presented a method for integrating the classical equations of motion of the atoms in a molecular system on ab initio potential surfaces.[5] Our method takes advantage of the fact that by using modern quantum chemical programs molecular gradients

---

(1) Polanyi, J. C. *Acc. Chem. Res.* 1972, *5*, 161–168.

(2) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.

(3) The amount of energy released in the form of relative motion of the two fragments will be termed translational energy release for reasons of simplicity. In many texts the term kinetic energy release is used for the same quantity.

(4) For a review, see: Derrick, P. J.; Donchi, K. F. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1983; Vol. 24, Chapter 2.

(5) Helgaker, T.; Uggerud, E.; Aa. Jensen, H. J. *Chem. Phys. Lett.* 1990, *173*, 145–150.

0002-7863/92/1514-4265$03.00/0 © 1992 American Chemical Society