Double-bond activation in unsaturated aldehydes: conversion of acrolein to propene and ketene on Pt(111) surfaces

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Abstract

The surface chemistry of acrolein on Pt(111) single-crystal surfaces was investigated under vacuum by temperature-programmed desorption (TPD) and reflection–absorption infrared spectroscopies (RAIRS). The main thermal decomposition path is via the decarbonylation of the unsaturated aldehyde to carbon monoxide and ethene, but it was found that small amounts of propene and ketene (CH_2CO) are also formed by following steps unprecedented in metal-based chemical systems. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

It has been well established that aldehydes can coordinate easily to transition-metal organometallic complexes via the activation of the formyl hydrogen and then undergo a facile decarbonylation step to yield the corresponding hydrocarbon [1–4]. Here we report a much less known process—the activation of the double bonds in α,β-unsaturated aldehydes. Specifically, experimental evidence is presented for the formation of both propene and ketene (CH_2CO) by thermal decomposition of acrolein on a Pt(111) surface. This in fact is a reaction that, to the best of our knowledge, has no precedence in either the organometallic or surface science fields.

2. Materials and methods

The experiments were performed in an ultra-high vacuum (UHV) chamber pumped to a base pressure below 10^{-10} Torr and equipped with an ion sputtering gun, an UTI-100C mass spectrometer for temperature-programmed desorption (TPD), and a Mattson Sirius 100 FT-IR spectrometer for reflection–absorption infrared spectroscopy (RAIRS) [5,6]. For the TPD experiments the mass spectrometer was controlled by a personal computer in a setup that allowed simultaneous data collection of up to 15 masses. A moveable cone was mounted in front of the quadrupole and ionizer to minimize the signals from both the sample holder and the back-

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ground gases. Only traces from selected masses are reported in Fig. 1, but several TPD experiments were performed for each set of conditions in order to obtain signals from a sufficient number of ion fragments to be able to unequivocally identify the desorbing products (by comparing with their cracking patterns). RAIRS was performed by focusing the IR beam from the spectrometer through a sodium chloride window onto the sample at grazing incidence, passing the reflected beam through a second sodium chloride window and a polarizer, and refocusing it into a mercury–cadmium–telluride (MCT) detector. The spectra presented in this paper correspond to the average of 1000 scans taken with 4 cm^{-1} resolution and ratioed against similarly-obtained spectra for the clean surface prior to dosing. The platinum single crystal was cut

in the (111) orientation and polished using standard procedures, and cleaned in situ before each experiment by sputtering–oxidation–annealing cycles. The acrolein was purchased from Aldrich (> 90% purity) and used as supplied, but the purity of its vapor was checked by mass spectrometry in the vacuum chamber before each experiment. Doses are reported in langmuirs (1 L = 10^{-6} Torr s), and were not corrected for the differences in ion gauge sensitivity.

3. Results

Fig. 1 displays TPD traces obtained after dosing the Pt(111) surface with 7.0 L of acrolein at 90 K. Several desorbing products were detected upon thermal activation of the chemisorbed acrolein, namely, carbon monoxide, ethene, hydrogen, propene, and ketene (CH_2CO). Carbon monoxide, the main product, is most likely the result of the decarbonylation step mentioned in the introduction. Its TPD peak represents a yield of about 0.30 monolayers, and is centered at 403 K, about the same temperature as that of CO on clean Pt(111) [7], which means that its detection is limited by the desorption step and that the surface reaction responsible for its production may take place at much lower temperatures. Ethylene is almost certainly formed via a β-hydride elimination from the ethyl moiety produced by that same reaction [8,9], but in this case its peak maximum at 330 K is indicative of the point at which the decarbonylation reaction occurs, because the subsequent ethyl dehydrogenation step is quite facile (it occurs below 300 K in ethyl surface groups [10]). Hydrogen desorbs in three stages about 290, 450, and 515 K, indicating that some of the adsorbed hydrocarbon fragments (probably some olefins) do not desorb but dehydrogenate in several steps and eventually yield surface carbon instead.

The most interesting observation from Fig. 1 is the fact that the thermal activation of acrolein on Pt(111) also leads to the production of small
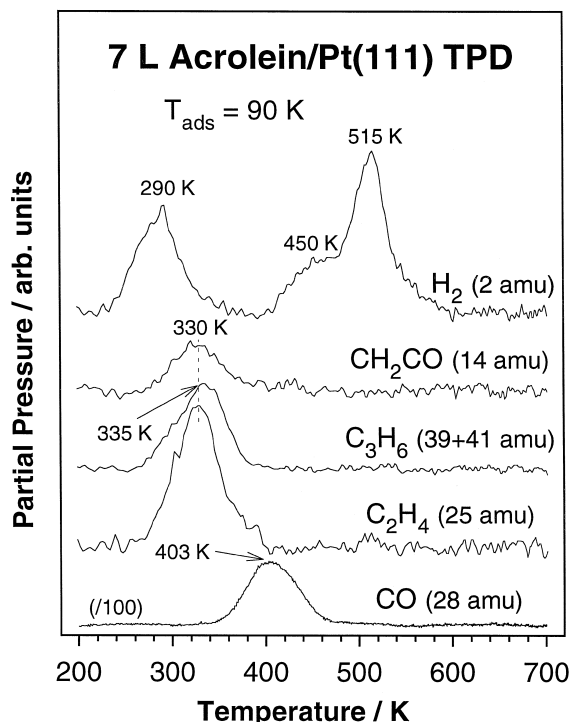

Fig. 1. Survey TPD spectra from 7.0 L of acrolein adsorbed on Pt(111) at 90 K. Five desorbing products were identified here, namely (from bottom to top), carbon monoxide, ethene, propene, ketene, and hydrogen. Notice in particular that propene and ketene production requires the unprecedented activation of the double bonds in the adsorbed acrolein.

amounts of propene and ketene. This is quite significant, because the formation of such molecules requires the scission of the C=O and C=C double bonds, respectively, and those steps are not expected at the low temperatures under which these reactions are observed. Also to notice is the fact that both products desorb at approximately the same temperature, about 335 and 330 K, respectively, suggesting that they are produced by the same mechanism. Finally, a more detailed coverage-dependence TPD study indicated that the reaction kinetics is most likely second-order in acrolein coverage, which means that the rate limiting step is bimolecular [11].

The TPD experiments were complemented by the characterization of the surface intermediates with RAIRS. Fig. 2 displays the vibrational spectra obtained from the platinum surface after

annealing 8.0 L of adsorbed acrolein to different key temperatures. The low-temperature (90 K) trace is similar to that seen for liquid acrolein [12], and therefore corresponds to the molecularly adsorbed species. However, the relative weak signal for the $\nu(CO)$ mode at 1700 cm^{-1} compared to that in the spectrum of pure acrolein suggests a flat-lying adsorption geometry, and the intensity seen around the low-frequency side of that feature argues for some isomerization to the *cis* conformer on the surface [11]. Significant changes are seen upon heating the sample. For one, the production of carbon monoxide is manifested by the appearance of the new bands at 1812 and 2054 cm^{-1} for CO coordinated to bridge and on-top sites on the platinum surface, respectively [13], which starts at 280 K and peaks at about 340 K (just before the onset of the CO desorption). Also, the two features at 1124 and 1341 cm^{-1} that begin to grow around 300 K and develop fully at 420 K identify the ethylidyne ($Pt_3{\equiv}C{-}CH_3$) moieties that form upon thermal activation of adsorbed ethylene [14,15]; they correspond to a coverage of about 0.25 monolayers [16], which once again indicates that the decarbonylation process is quite efficient and dominates the thermal chemistry of acrolein on Pt(111). Finally, the two additional peaks at 1698 and 1725 cm^{-1} that are seen in the 280 K trace can be assigned at least in part to a η^2(C,C)-coordinated ketene [17]. Notice that the ketene IR features grow at the onset of its TPD peak (about 260 K), and disappear once the desorption is complete (before 330 K). No vibrational signals could be detected for propene, but this is not surprising given both the low infrared absorption cross-sections for those modes [18] and the low yield of that product in the acrolein system.
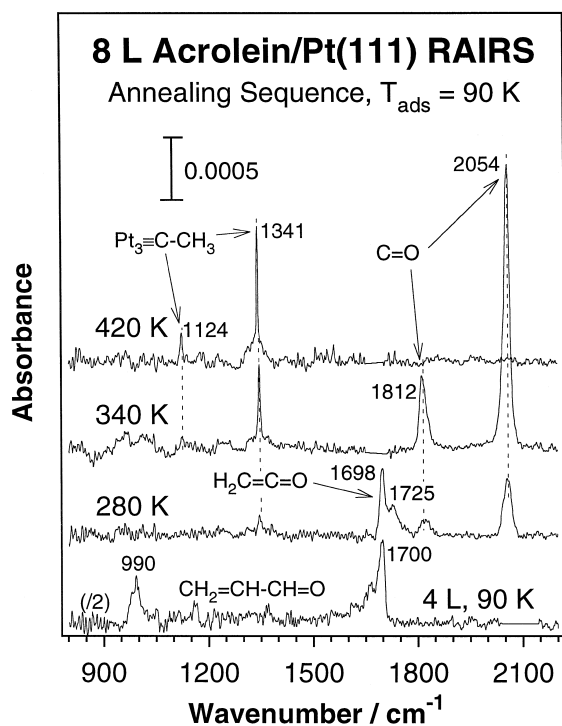

Fig. 2. RAIRS spectra from 8.0 L of acrolein on Pt(111), adsorbed at 90 K and heated to the indicated temperatures. Several surface species are identifiable in these data, including the ketene (and perhaps an acrolein dimer) responsible for the two peaks at 1698 and 1725 cm^{-1} in the 280 K trace. An initial dimerization of acrolein is also suggested by its flat *cis* conformation on the surface at 90 K.

4. Discussion

It is interesting to speculate on the possible mechanism for the activation of the double

Proposed Mechanism for the Decomposition of Acrolein on Pt(111)
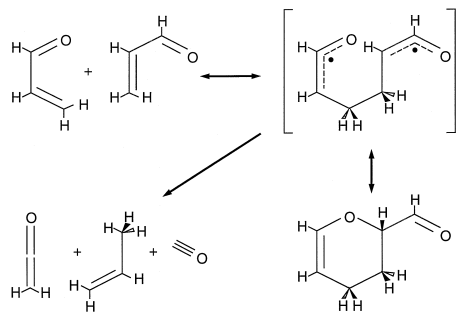
Scheme 1.

bonds in acrolein when chemisorbed on Pt(111). Reduction of acrolein to propene has been seen on platinum electrodes in acid media [19], and propene desorption has also been detected in TPD experiments with allyl alcohol on Pd(111) [20], but a similar process in our case would require the unlikely initial hydrogenation of the C=O bond [21], and would still not account for the concurrent formation of CH_2CO. Instead, we propose an initial Diels–Alder condensation, a process that is known to occur easily in solution [22]. Four pieces of evidence can be offered at this point to support this mechanism: (1) acrolein dimerization would be favored by its flat cis adsorption geometry on the Pt(111) surface; (2) some of the signal in the 280 K IR spectrum around 1700 cm^{-1} could originate from the dimer; (3) propene and CH_2CO appear to form from the same reaction; and (4) the dimerization reaction is consistent with the second-order kinetics seen in TPD. The condensation initial step could then be followed by decarbonylation of the end aldehyde group and cracking of the remaining 3,4-dihydro-2 *H*-pyran six-membered heterocycle, or perhaps by direct fragmentation of the biradical-like intermediate formed during the initial dimerization (Scheme 1). Isotope labelling experiments will be perform to test this hypothesis.

Acknowledgements

References

[1] J. Tsuji, K. Ohno, Synthesis 157 (1969) 1.
[2] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, 1987.
[3] J. Tsuji, K. Ohno, Tetrahedron Lett. (1970) 823.
[4] W.H. Walborsky, L.E. Allen, J. Am. Chem. Soc. 93 (1971) 5465.
[5] H. Hoffmann, P.R. Griffiths, F. Zaera, Surf. Sci. 262 (1992) 141.
[6] T.V.W. Janssens, F. Zaera, J. Phys. Chem. 100 (1996) 14118.
[7] G. Ertl, M. Neumann, K.M. Streit, Surf. Sci. 64 (1977) 393.
[8] F. Zaera, J. Am. Chem. Soc. 111 (1989) 8744.
[9] F. Zaera, Chem. Rev. 95 (1995) 2651.
[10] F. Zaera, Surf. Sci. 219 (1989) 453.
[11] J.C. de Jesús, F. Zaera, 1997, to be published.
[12] F. Bournel, C. Laffon, P. Parent, G. Tourillon, Surf. Sci. 359 (1996) 10.
[13] M. Xu, J. Liu, F. Zaera, J. Chem. Phys. 104 (1996) 8825.
[14] P. Skinner, M.W. Howard, I.A. Oxton, S.F.A. Kettle, D.B. Powell, N. Sheppard, J. Chem. Soc., Faraday Trans. 2 77 (1981) 1203.
[15] F. Zaera, Langmuir 12 (1996) 88.