and isotropic and anisotropic thermal parameters (15 pages); listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Methanolic C–O Bond Activation on Pd{111}: A Coverage-Dependent Reaction

Jr-Jyan Chen and Nicholas Winograd*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

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We find that the previously reported methanolic C–O bond activation on Pd{111} to form adsorbed methyl and hydroxyl at 225 K[1] occurs only for initial methanol coverages near 1 monolayer. At lower and higher coverages, methanol decomposes via the more traditional methoxy intermediate. Moreover, when methyl is formed, it is not observed to decompose until the temperature is raised to 400 K. This thermal behavior is quite unusual since CH_3 has been observed to combine with H to desorb as CH_4 below 300 K,[2-5] dimerize to produce C_2H_6 below 200 K,[6,7] or dehydrogenate to form CH_2 and H below 200 K.[8] In addition, we find that methyl undergoes sequential dehydrogenation as the temperature is increased to form CH_2 at 400 K, CH at 500 K, and C at >500 K. We speculate that the coverage dependency is connected with the thermal stability of CH_3 by a site-blocking mechanism, probably involving CO.

Although methylidyne, methylene, and methyl have been proposed to be the fundamental building units in catalytic methanation and Fischer–Tropsch synthesis,[9,10] direct evidence of such radicals on a well-defined single crystal under ultrahigh vacuum conditions is sparse.[1,8,11-13] Using X-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS), we previously reported direct evidence for CH_3 and OCH_3 formation on Pd{111} during CH_3OH decomposition after initial exposures of ~1.25 L (1 L = 10^{-6} Torr s),[1] where 1 monolayer corresponds to ~1.3-L exposure. These conclusions were questioned in subsequent work from data produced by a series of isotope scrambling experiments which showed that the CO bond remained intact during methanol decomposition.[14] Many other confusing reports concerning the reactivity of simple hydrocarbons abound in the literature,[15-18] and it is important to establish the experimental parameters which allow the critical mechanistic pathways to emerge.

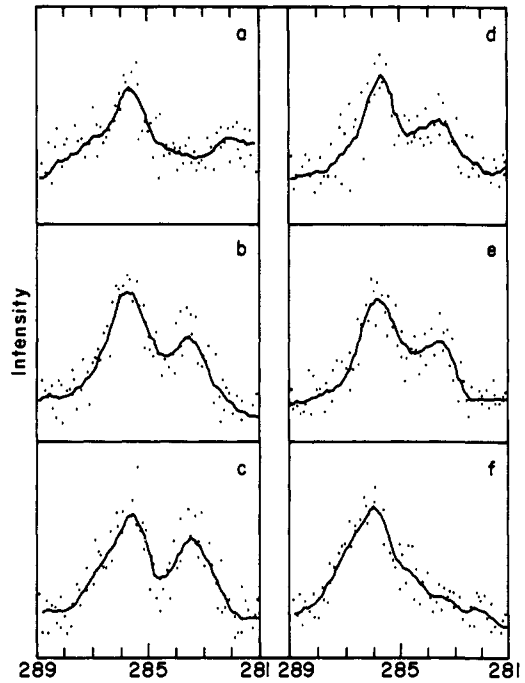

Figure 1. Carbon 1s XPS spectra for Pd{111} exposed to (a) 0.75 L, (b) 1.00 L, (c) 1.25 L, (d) 1.50 L, (e) 1.75 L, and (f) 2.00 L of methanol at 105 K and then heated to 300 K. The spectra are reported without normalization.

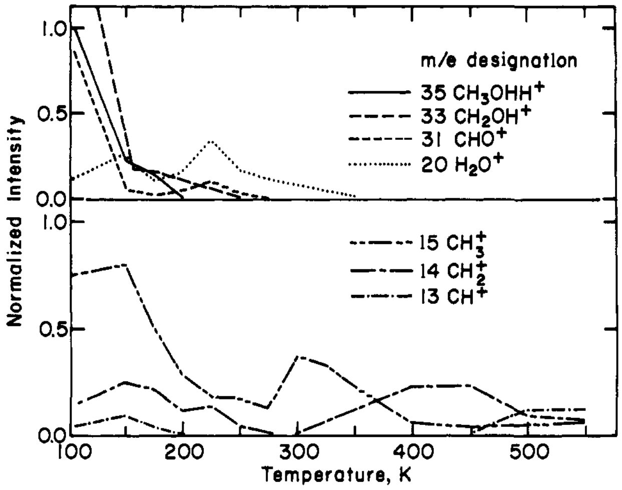

Figure 2. Intensity of selected positive secondary ions versus surface temperature for Pd{111} exposed to 1.25 L of $CH_3{}^{18}OH$ initially at 105 K. The ion intensities are determined from peak heights and reported relative to the $CH_3{}^{18}OHH^+$ ion signal at 105 K. Spectra were recorded with an Ar^+ ion beam energy of 3.0 KeV and an ion beam current density of 2 nA/cm^2.

Experiments were conducted in a multitechnique surface analysis system described previously.[19] The procedures for cleaning a Pd{111} crystal and purifying methanol and the spectroscopic protocols involving binding-energy referencing, peak deconvolution, and static SIMS measurements have been described in detail.[1] Methanol exposures are corrected by an ion gauge sensitivity factor of 1.9.[20] All spectra were recorded after the sample was warmed to the desired temperature at ~1 K/s and recooled to near the adsorption temperature of 105 K.

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(1) Levis, R. J.; Jiang, Z.; Winograd, N. *J. Am. Chem. Soc.* **1988**, *110*, 4431; **1989**, *111*, 4605.

(2) Steinbach, F.; Kiss, J.; Krall, R. *Surf. Sci.* **1985**, *157*, 401.

(3) Zhou, X. L.; Yoon, C.; White, J. M. *Surf. Sci.* **1988**, *206*, 379.

(4) Benziger, J. B.; Madix, R. J. *J. Catal.* **1980**, *65*, 49.

(5) Henderson, M. A.; Mitchell, G. E.; White, J. M. *Surf. Sci.* **1987**, *184*, L325.

(6) Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1986**, *108*, 2881.

(7) Zhou, X. L.; Solymosi, F.; Blass, P. M.; Cannon, K. C.; White, J. M. *Surf. Sci.* **1989**, *219*, 294.

(8) Lee, M. B.; Yang, Q. Y.; Tang, S. L.; Ceyer, S. I. *J. Chem. Phys.* **1986**, *85*, 1693.

(9) Bell, A. T. *Catal. Rev.—Sci. Eng.* **1981**, *23* (1, 2), 203.

(10) Lee, G. v. d. *Catal. Rev.—Sci. Eng.* **1987**, *29* (2, 3), 183.

(11) Kaminsky, M. P.; Winograd, N.; Geoffroy, G. L.; Vannice, M. A. *J. Am. Chem. Soc.* **1986**, *108*, 1315.

(12) George, M. P.; Avery, N. R.; Weinberg, W. H.; Tebbe, F. N. *J. Am. Chem. Soc.* **1983**, *105*, 1393.

(13) Demuth, J. E.; Ibach, H. *Surf. Sci.* **1978**, *78*, L238.

(14) Guo, X.; Yates, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 3155.

(15) Kruse, N.; Rebholz, M.; Matolin, V.; Chuah, G. K.; Block, J. H. *Surf. Sci.* **1990**, *238*, L457.

(16) Wang, J.; Masel, R. I. *J. Am. Chem. Soc.* **1991**, *113*, 5850.

(17) Rebholz, M.; Kruse, N. *J. Chem. Phys.* **1991**, *95*, 7745.

(18) Solymosi, F.; Révész, K. Submitted to *J. Am. Chem. Soc.*

(19) DeLouise, L.; Winograd, N. *Surf. Sci.* **1984**, *138*, 417.

(20) Summers, R. L. NASA Technical Note TND-5285; **1969**.

Figure 1 shows the C 1s photoelectron spectra for a clean Pd{111} sample exposed to a series of different methanol exposures at 105 K and subsequently heated to 300 K. The peaks with BEs of 285.8 and 283.8 eV are assigned to OCH_3 and CH_3, respectively.[1] The formation of CH_3 exhibits a striking dependence on the initial coverage of methanol, forming only between exposures of 1.00 and 1.75 L. This requirement suggests that there is a specific arrangement of methanol molecules occurring near monolayer coverage on the Pd surface which is required to activate the C–O bond, perhaps involving hydrogen bonding between OH units of adjacent methanol molecules.[21] Although the details of the initial coverage effect is still an open question, the observation would certainly explain the variability of results obtained with this seemingly straightforward model system.

The temperature dependence of CH_3 formed by a 1.25-L exposure of methanol to Pd{111} at 105 K is striking. The methanol itself remains molecularly adsorbed until the temperature is increased to 225 K. At this point, the single C 1s peak at 286.2 eV splits into two peaks at 285.8 and 283.8 eV as noted above. Thereafter, the surface OCH_3 and CH_3 species undergo two independent reaction channels. The high binding energy peak shifts slightly, to 286.0 eV, by 400 K, suggesting decomposition of OCH_3 to CO and H_2. Above 400 K, CO and H_2 desorption is observed, accompanied by a gradual shift of the 283.8-eV peak toward 285.0 eV. This trend suggests that the CH_3 species is undergoing a decomposition reaction, presumably involving dehydrogenation, where the products are characterized by using SIMS as discussed below.

The positive-ion SIMS peak intensities as a function of temperature after exposing Pd{111} 1.25 L of $CH_3{}^{18}OH$ at 105 K are shown in Figure 2. The intensities of methanol ions (m/e = 35, 33, 31) and $CH_x{}^+$ ions decline concurrently as the temperature is increased from 105 to 275 K. This result indicates that in this temperature range molecularly adsorbed methanol either desorbs or decomposes into other species. When the surface temperature reaches 300 K, however, the $CH_3{}^+$ ion intensity increases and $CH_3{}^+$ is the major carbon-containing secondary ion. This ion correlates with the XPS C 1s peak at 283.8 eV seen in Figure 1 and is associated with CH_3. Note the development of secondary ions with m/e 14 and 13 at 400 and 500 K, respectively, which eventually ends up with a mixed phase of CH_x (x = 0–3) at 550 K. The appearance of CH_x ($x < 3$) secondary ions is consistent with the XPS C 1s peak shift from 283.8 to 285.0 eV and indicates that a stepwise dehydrogenation of CH_3 occurs at $T \geq 400$ K. This unusual stability of CH_3 on the Pd{111} is generally not found on clean metal surfaces above 300 K. In our case, however, the CH_3 species is stable to the temperature where CO begins to desorb from the surface. Hence, it is possible that CO chemisorption may block the dehydrogenation or recombination of CH_3. A similar site-blocking mechanism has been observed for C_2 fragments coadsorbed with CO on Ni{001} and Ru{001}.[22]

We believe that the results presented here are important for several reasons. (1) The formation of CH_3 from CH_3OH is found to occur over a very limited initial coverage of methanol. This observation implies that the formation of CH_3 is contingent upon a special molecular arrangement of precursors before reaction and that the CH_3 product is stabilized by ancillary reaction products, such as CO. (2) The dramatic dependence of the reaction pathway on initial reaction conditions helps to explain divergent observations from other laboratories. (3) The combination of XPS and SIMS provides a unique approach for examining the fate of these important reaction intermediates.

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Registry No. Methanol, 67-56-1; palladium, 7440-05-3.

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[21] Peremans, A.; Maseri, F.; Darville, J.; Gilles, J.-M. *Surf. Sci.* **1990**, *227*, 73.

[22] Akhter, S.; Henderson, M. A.; Mitchell, G. E.; White, J. M. *Langmuir* **1988**, *4*, 246.

New Intermediates Observed in the Flash Photolysis of $Cp_2Fe_2(CO)_4$

Shulin Zhang and Theodore L. Brown*

School of Chemical Sciences
University of Illinois at Urbana—Champaign
Urbana, Illinois 61801

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The photochemistry of $Cp_2Fe_2(CO)_4$, **1**, has received a great deal of attention.[1-7] Both CO loss and metal–metal bond homolysis are established as primary photochemical pathways.[2,4,5] The CO loss species of symmetrical structure, $Cp_2Fe_2(\mu\text{-}CO)_3$, **2**, is the most thoroughly established intermediate.[1b,5c] Other than that it is formed exclusively from the trans isomer and not seen within 1 ns following 580-nm laser excitation,[6b] nothing is known of the mechanism or kinetics of its formation. We have investigated the photochemistry of **1** in hydrocarbon solution, using conventional xenon flash and laser flash photolysis, at both room temperature and low temperatures. We report here the existence of three previously unreported intermediates, and observations that indicate the origin and fate of each.

Xenon flash lamp irradiation of a hexane solution of **1** at room temperature under Ar results in the appearance of **2** (λ_{max} = 510 nm), which decays with second-order kinetics. However, the absorbance at 510 nm does not return to the original value within 8 s. The UV–visible spectrum of the solution taken within 20–30 s following the flash (by which time **2** has disappeared) reveals the presence of a longer-lived species ($\lambda_{max} \approx 380$ nm). The difference IR spectrum, taken after **2** has disappeared, reveals negative absorbances due to **1** and three new bands (1839, 1786, 1674 cm^{-1}) which disappear over 2–3 h (Figure 1a). Several isosbestic points are observed, showing that the new species, designated **3**, decays to form **1**. **3** is not observed following photolysis in solutions under CO.

Sunlamp irradiation (predominantly 366 nm) causes rapid loss of **3** to form **1**. The IR spectrum of **3** is consistent with a semibridged species, as shown in Scheme I. Making allowance for the presence of an additional terminal CO on each metal in the Mo species, the observed pattern of bands is closely similar to that ascribed to $Cp_2Mo_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ (1978, 1933, 1898, 1855, and 1665 cm^{-1}).[5b,8]

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[1] (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (b) Hepp, A. F.; Blaha, J. P.; Lewis, C.; Wrighton, M. S. *Organometallics* **1984**, *3*, 174.

[2] (a) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7794. (b) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

[3] (a) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753. (b) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 6018. (c) Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253. (d) Castellani, M. P.; Tyler, D. R. *Organometallics* **1989**, *8*, 2113. (e) Tyler, D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 338.

[4] (a) Moore, B. D.; Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1984**, 972. (b) Moore, B. D.; Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Phys. Chem.* **1985**, *89*, 850. (c) Dixon, A. J.; Healy, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1986**, 994. (d) Moore, B. D.; Poliakoff, M.; Turner, J. *J. Am. Chem. Soc.* **1986**, *108*, 1819. (e) Dixon, A. J.; Gravelle, S. J.; van de Burgt, L. J.; Poliakoff, M.; Turner, J. J.; Weitz, E. *J. Chem. Soc., Chem. Commun.* **1987**, 1023.

[5] (a) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022. (b) Hooker, R. H.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1221. (c) Bloyce, P. E.; Campen, A. K.; Hooker, R. H.; Rest, A. J.; Thomas, N. R.; Bitterwolf, T. E.; Shade, J. E. *J. Chem. Soc., Dalton Trans.* **1990**, 2833.

[6] (a) Moore, J. N.; Hansen, P. A.; Hochstrasser, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 4563. (b) Anfinrud, P. A.; Han, C.-H.; Lian, T.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 574.

[7] (a) Bursten, B. E.; Cayton, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 8241. (b) Bursten, B. E.; Mckee, S. D.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 3428.

[8] Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Organomet. Chem.* **1983**, C25.

0002-7863/92/1514-2723$03.00/0