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Thermal Decomposition of Chemisorbed Azomethane on Pd(111)

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(Received: December 27, 1988)

The adsorption and thermal decomposition of azomethane ($CH_3N{=}NCH_3$) on Pd(111) under ultrahigh-vacuum conditions was studied by temperature-programmed desorption and work function measurements. Adsorbed azomethane is stable on the surface until N–N bond scission occurs at ~250 K. Above 280 K, further decomposition forms H(a) and HCN(a) which subsequently desorb at higher temperatures. No C–N bond dissociation is observed on Pd(111). Thus, both N–N and C–H bond cleavages are observed for chemisorbed azomethane on Pd(111), while only C–N bond cleavage is observed in the gas-phase thermal decomposition of azomethane.

Introduction

The photochemistry of molecules adsorbed on single-crystal surfaces has become the focus of several recent experiments.[1] For a molecule to be considered in surface photochemical studies, both its gas-phase photolysis and its surface thermochemistry and kinetics must be well characterized. Azomethane fits the first criterion, since it is known to photolyze under irradiation with UV or visible light.[2] The adsorption behavior of azomethane has only been briefly studied on Pt(111),[3] and no studies have been made of azomethane on Pd surfaces. We have therefore examined its adsorption and thermal decomposition on Pd(111). The results presented here also serve as a preface to photochemical studies which are presently under way.

Azomethane, $CH_3N{=}NCH_3$, was shown by dipole moment experiments[4] to be entirely in the trans configuration in the gas phase. Electron diffraction studies[5] verified this geometry and also measured the interatomic distances and angles. In the gas phase, azomethane thermally decomposes above ~500 K to N_2 and CH_3 radicals; the latter then scavenge hydrogen or methyl groups from other azomethane molecules to form methane and ethane.[6] One would expect azomethane to bond to a transition-metal surface through the N–N π-bond.[7] Adsorption of the molecule in this fashion would be expected to alter the surface-catalyzed thermal chemistry significantly from the gaseous thermal decomposition. As will be shown below, thermal decomposition on the surface does differ fundamentally from that in the gas phase.

Experimental Details

The experimental apparatus has been described in detail previously[8] and will only be briefly discussed here. The stainless steel ultrahigh-vacuum system (base pressure 1×10^{-10} Torr) was equipped for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), work function measurements ($\Delta\phi$, by Kelvin probe), and temperature-programmed desorption (TPD) with a differentially pumped, apertured quadrupole mass spectrometer. The Pd(111) surface was dosed with azomethane either by a calibrated and collimated effusive molecular beam doser[9] (during TPD and AES) or by system doses (during $\Delta\phi$ measurements). System doses were calibrated with a nude Bayard Alpert ionization gauge, assuming the ionization efficiency of azomethane is equal to that of N_2. For TPD measurements, the crystal was resistively heated at a rate of 2 K/s and cooled by liquid nitrogen to 87 K. The Kelvin probe was calibrated by measuring the known $\Delta\phi$ for a saturation coverage of CO on clean Pd(111),[10] and the error in $\Delta\phi$ was within 0.07 eV. The Pd(111) was oriented by Laue X-ray diffraction, polished, and cleaned in vacuo by Ar^+ sputtering and oxygen treatments, as previously detailed.[11,12]

(1) See, for example: Costello, S. A.; Roop, B.; Liu, Z.-M.; White, J. M. *J. Phys. Chem.* **1988**, *92*, 1019. Harrison, I.; Polanyi, J. C.; Young, P. A. *J. Chem. Phys.* **1988**, *89*, 1475. Marsh, E. P.; Schneider, M. R.; Gilton, T. L.; Tabares, F. L.; Meier, W.; Cowin, J. P. *Phys. Rev. Lett.* **1988**, *60*, 2551. Grassian, V. H.; Pimentel, G. C. *J. Chem. Phys.* **1988**, *88*, 4484. Celii, F. G.; Whitmore, P. M.; Janda, K. C. *Chem. Phys. Lett.* **1987**, *138*, 257. Germer, T. A.; Ho, W. *J. Chem. Phys.* **1988**, *89*, 562.

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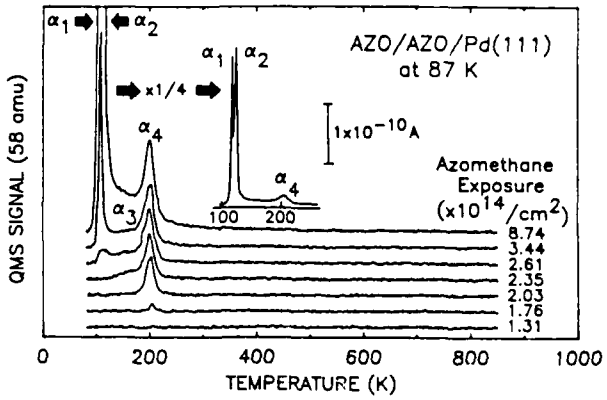

Figure 1. TPD spectra of azomethane (58 amu) desorbing from Pd(111) for increasing azomethane exposures at 87 K.

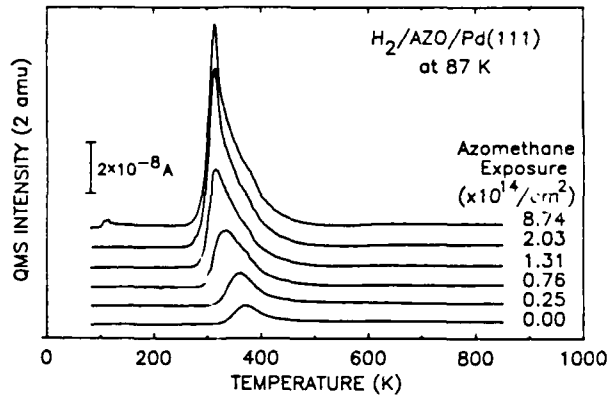

Figure 2. TPD spectra of H_2 (2 amu) desorbing from Pd(111) for increasing azomethane exposures at 87 K.

Azomethane was prepared by the method of Jahn.[13] First, the $[CH_3N{=}NCH_3][CuCl_2]$ complex was synthesized by oxidation of *sym*-dimethyldihydrazine (Sigma Chemical Co.) with sodium acetate in aqueous cupric chloride.[14] Next, azomethane was liberated from the complex by heating in a glass vacuum line (base pressure 2×10^{-6} Torr) and collected in a dry ice–acetone (196 K) cooled bulb. Azomethane was always sampled from the vapor above the dry ice–acetone cooled mixture of water, azomethane, and other possible condensed impurities, after several freeze–pump–thaw cycles in liquid nitrogen. The purity was checked by both high-resolution mass spectroscopy and the low-resolution QMS in the UHV chamber. Slight contamination (<1%) of methyl chloride, with unique mass spectral features at 50 and 52 amu, was occasionally found in the azomethane. This necessitated the preparation of a clean azomethane sample, since even slight CH_3Cl impurities significantly altered the surface chemistry. Attempts to separate methyl chloride and azomethane by fractional distillation were unsuccessful.

Results and Interpretation

Temperature-Programmed Desorption. Temperature-programmed desorption (TPD) was performed first to elucidate the desorption features and decomposition products of azomethane on Pd(111). The Pd(111) was dosed with azomethane at 87 K, and the QMS was multiplexed for all possible desorption products from 2 to 80 amu. The only desorbing species observed are azomethane (58 amu), H_2 (2 amu), and HCN (27 amu), as shown in Figures 1–3, respectively. Previous experience[12] has shown that atomic carbon, produced by various decomposition processes involving organic adsorbates, cannot be desorbed from the Pd(111) surface while atomic hydrogen and nitrogen desorb as H_2 and N_2, respectively. No CO or CO_2 desorption resulted from oxygen titration[12] of the Pd(111) surface after a single azomethane de-

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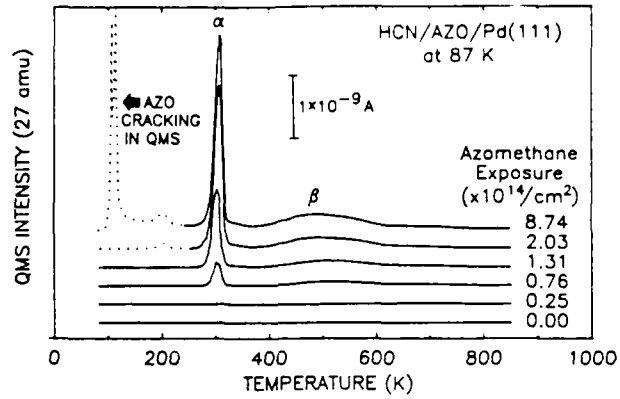

Figure 3. TPD spectra of HCN (27 amu) desorbing from Pd(111) for increasing azomethane exposures at 87 K.

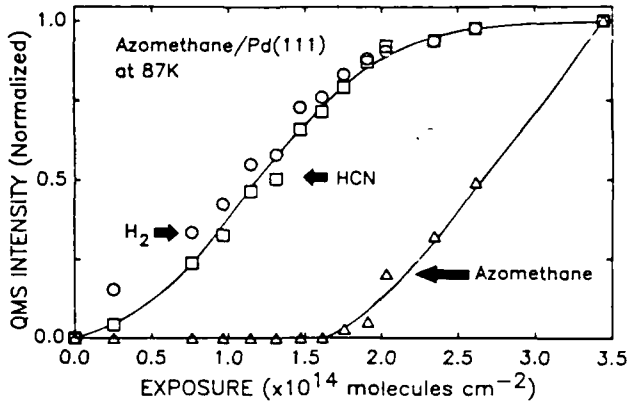

Figure 4. Relative yields of H_2, HCN, and azomethane for increasing exposures of azomethane at 87 K on Pd(111).

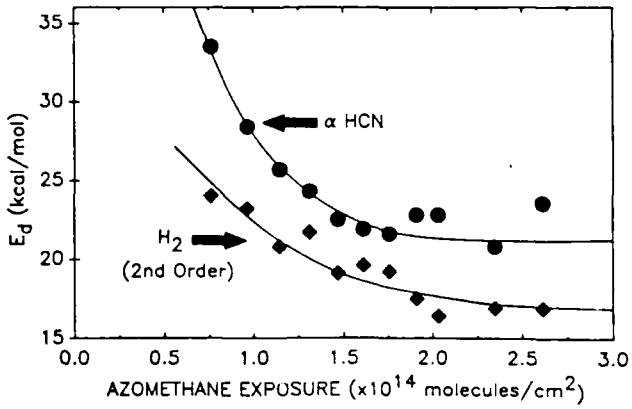

Figure 5. Change in desorption activation energy (E_d) of H_2 and α-HCN for increasing azomethane exposure.

sorption experiment, indicating that adsorbed carbon is not a product of azomethane surface decomposition. Furthermore, since no N_2 was observed to desorb, it was concluded that adsorbed nitrogen was not produced by the decomposition of azomethane.

Figure 4, a plot of exposure versus coverage for all three desorption species, shows that at low exposures only H_2 and HCN desorb. With increasing exposures, the H_2 and HCN yields first reach saturation and then molecular azomethane is observed as a desorption product. The TPD behavior indicates that azomethane clearly decomposes at some temperature below ~300 K.

Figures 2 and 4 show that the H_2 (2 amu) desorption displays a desorption feature whose area increases until saturation at an exposure of $\sim 3 \times 10^{14}$ molecules/cm^2 of azomethane. The peak desorption temperature, T_p, of this hydrogen shifted from 361 K at lowest dose to 314 K at the highest dose. Figure 5 shows that the hydrogen desorption activation energy (E_d) shifted from 25 kcal/mol at low exposure to 17 kcal/mol at high exposure, as

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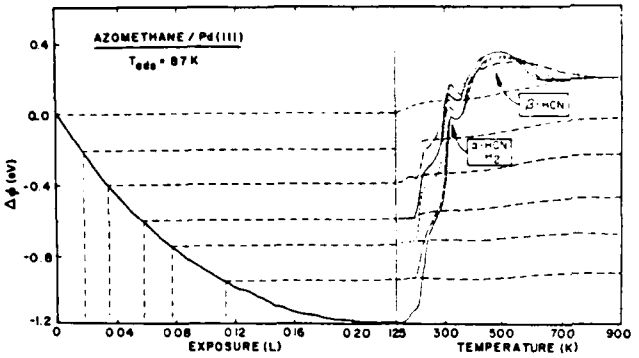

Figure 6. Work function change upon adsorption of azomethane on Pd(111) at 87 K (left) and during desorption (right).

calculated by a second-order, leading edge kinetic analysis.[15] The rapid decomposition near 300 K to produce atomic hydrogen could also generate dissolved hydrogen. Dosing clean Pd(111) with H_2 always produces small quantities of dissolved hydrogen even at low temperatures.[16] The small H_2 peak at 361 K observed with no azomethane exposure in Figure 2 resulted from adsorption of background hydrogen.

Figure 3 shows that HCN (27 amu) desorbed in two processes: α-HCN at 308 K (E_d = 21 kcal/mol) and β-HCN at 479 K (E_d = 34 kcal/mol). The α-HCN and H_2 desorption yields are observed to saturate simultaneously. The constant T_p with changing coverage for α-HCN suggests first-order desorption kinetics which result from a rate-controlling step due to a molecular species, whereas the shifting T_p for β-HCN suggests second desorption order kinetics which result from a recombination process. It therefore appears that α-HCN corresponds to the desorption of molecular HCN while β-HCN corresponds to recombination of adsorbed hydrogen with surface CN. A similar (H + CN → HCN) recombination process has been previously observed in the same temperature range.[12] At an azomethane coverage corresponding to the first appearance of azomethane desorption, 27 amu desorption features appeared below 250 K corresponding to the cracking of desorbing azomethane during electron impact ionization in the QMS.[17] This is shown by the dotted curves in Figure 3.

Azomethane (58 amu) desorbed from Pd(111) molecularly in four distinct processes, as shown in Figure 1:

$$\alpha_1:\quad T_p = 106\ \text{K},\ E_d = 6.4\ \text{kcal/mol}$$

$$\alpha_2:\quad T_p = 114\ \text{K},\ E_d = 6.9\ \text{kcal/mol}$$

$$\alpha_3:\quad T_p = 156\ \text{K},\ E_d = 9.5\ \text{kcal/mol}$$

$$\alpha_4:\quad T_p = 201\ \text{K},\ E_d = 12.4\ \text{kcal/mol}$$

where the values of E_d were calculated from T_p, via the Redhead equation, assuming a first-order process with $\nu = 10^{13}\ \text{s}^{-1}$. Since T_p did not shift with azomethane exposure for any of the α peaks, it appeared that the α_2, α_3, and α_4 desorption processes were first order and, therefore, correspond to direct desorption of molecular azomethane. The α_2, α_3, and α_4 desorption processes saturated after a dose of 3.4×10^{14} azomethane molecules/cm^2, which (given a Pd atom surface density of 1.534×10^{15} atoms/cm^2 and a sticking probability of $s = 1$) corresponds to a coverage of ~0.25 monolayer. However, the similarity of E_d for α_1 and α_2 indicates that the latter may correspond to desorption of a second layer, and we cannot unambiguously determine whether α_2 results from desorption of the first or second adsorbate layer. For higher doses, the α_1 desorption yield increased linearly with exposure after all

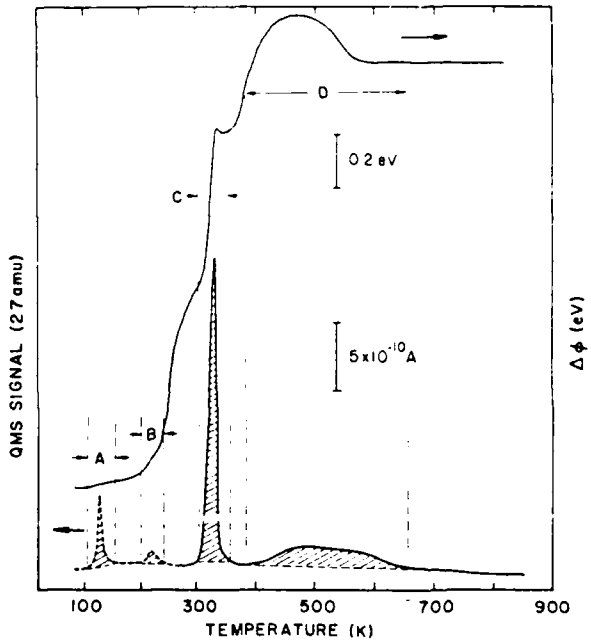

Figure 7. Comparison of the HCN TPD spectrum with work function change during desorption for equal exposures of azomethane at 87 K. Exposure = 4×10^{14} molecules/cm^2.

other desorption yields have saturated, indicating that α_1-azomethane resulted from desorption from the azomethane multilayer.

Work Function Measurements (Δφ). The most important conclusion which was drawn from the Δφ measurements is that azomethane did not decompose on the surface until ~250 K. Figure 6 shows Δφ both during adsorption of azomethane by system doses at 87 K and during desorption by TPD. While Δφ decreased monotonically with azomethane adsorption, during desorption the increase in Δφ was structured with features correlated to the TPD spectra, as shown in Figure 7. This is clear evidence that, during TPD, there were thermally induced changes in the chemisorbed layer which did not occur during the low-temperature adsorption. Figure 6 also reveals that the general shape and temperature dependence of $\Delta\phi[T(t)]$ is independent of coverage, thus indicating that the chemical processes occurring on the surface are essentially the same, regardless of azomethane exposure.

In Figure 7, the $\Delta\phi[T(t)]$ dependence during desorption is compared with the HCN TPD spectrum: all but one of the regions of maximum change in Δφ (regions A, B, C, and D of Figure 7) correspond directly with TPD features. *The notable exception is the region from 240 to 300 K (between region B and region C) where the low rate of desorption of any products is far too small to justify the large Δφ.* This Δφ region is a result of the decomposition of the azomethane on the surface, probably by scission of the N–N bond. The large Δφ from ~300 to 320 K (Figure 7) is accompanied by H_2 and HCN desorption and results from a combination of C–H bond scission and product desorption. The change in Δφ sign from −0.2 to +0.2 eV over the temperature range 350–460 K (Figures 6 and 7) was accompanied by H_2 and β-HCN desorption. The positive Δφ probably results from CN on the surface. That the α_1- and α_2-azomethane desorption processes changed the work function by less than 0.1 eV is further indication that these desorption processes result from multilayer and second-layer azomethane, respectively.

Auger Measurements. While surface carbon could not be monitored on Pd by AES due to the overlap of the C(*KLL*) peak at 272 eV with the intense Pd(*MNN*) peak at 279 eV, no such interference is present with nitrogen. Control measurements showed that the influence of electron bombardment on the N(*KLL*) Auger spectrum of adsorbed azomethane was insignificant for the electron beam exposure times employed here. We believe the results presented below represent a reasonable qualitative assay of the nitrogen coverage on the surface, independent of whether

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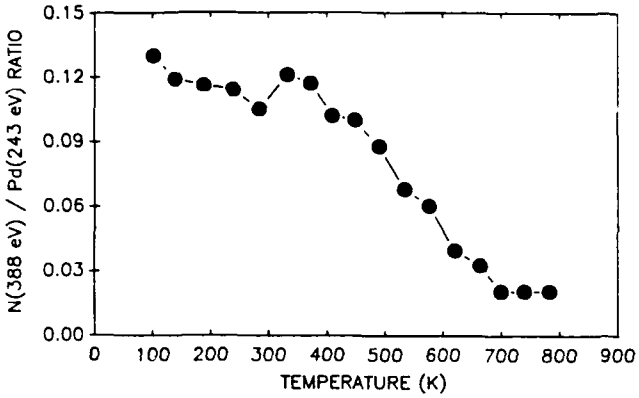

Figure 8. Change in Auger peak-to-peak ratio N(*KLL*)/Pd(*MNN*) during desorption and decomposition of azomethane, H_2, and HCN.

electron beam degradation of the azomethane is occurring during the measurement at a given temperature.

Auger measurements were made during sequential heating of an azomethane layer from 87 K, and the results are shown in Figure 8. Over the entire temperature range from 87 to 900 K, we did not observe any change in the N(*KLL*) line shape (388 eV). The peak-to-peak intensity ratio of N(*KLL*)/Pd(*MNN*) (at 388 and 243 eV, respectively) was taken as a measure of the nitrogen coverage on the surface, as shown in Figure 8. From 87 to 280 K, the N/Pd ratio continuously decreased as molecular azomethane was desorbed. At 310 K, there was an increase in the N/Pd ratio as H_2 and HCN desorbed. This anomalous increase could be related to either the N–N bond cleavage or a reduction in scattering of the Auger electrons by surface adsorbates (now depleted by desorption). Above 310 K, the N/Pd ratio continuously decreased as HCN was desorbed until it reached a minimum of 0.03, due to a small background Pd Auger peak at 388 eV.

LEED. A sharp (1×1) LEED pattern characteristic of a clean Pd(111) crystal was measured before azomethane adsorption. Upon adsorption of azomethane, the (1×1) pattern remained unchanged except for the appearance of a diffuse background, due to scattering of the reflected electrons by the disordered adsorbate layer. Neither annealing at 200 K nor variations in surface coverages changed these patterns. It was concluded that azomethane did not form an ordered overlayer on Pd(111) and the Pd atoms did not reconstruct during the adsorption.

Discussion

Mechanism of Azomethane Thermal Decomposition. From these experiments, the mechanism of azomethane adsorption and thermal decomposition has been partially deduced and is shown schematically in Figure 9. When Pd(111) is dosed with azomethane at 87 K, first a monolayer bonding through the N–N π-bond forms and then a multilayer of molecular azomethane adsorbs. None of the azomethane monolayer or multilayer decomposes at 87 K. As the crystal is heated to 900 K, first desorption of the multilayer (α_1 and possibly α_2 at 106 and 134 K) occurs. This is followed by desorption of the more strongly bound azomethane states up to ~200 K. Around 250 K, the N–N bond of the remaining adsorbed azomethane begins to break. Near 280 K, the adsorbed CH_3N species further decompose, by C–H bond breakage. The resulting hydrogen atoms and HCN desorb as the crystal temperature increases. At higher coverages, the surface coverage of hydrogen atoms released by the C–H decomposition is greater than can be bound by the surface at this temperature; so the H_2 desorption is essentially instantaneous. Part of the HCN desorbs and part decomposes at 340 K to H and CN species, which recombine and desorb above 350 K. Previous studies[18] indicated that the horizontal configuration of CN with respect to the surface is preferred. By 800 K, the Pd(111) surface is completely clean.

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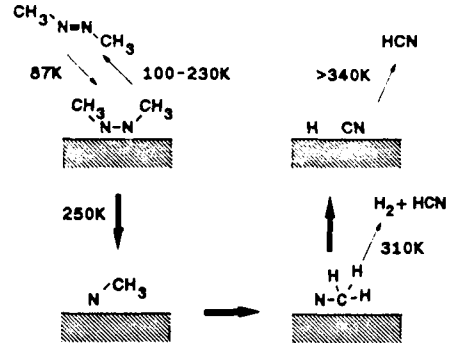

Figure 9. Proposed decomposition mechanism for adsorbed azomethane on Pd(111). See text for further explanation.

Energetics of Azomethane Decomposition. In the gas phase, the decomposition of azomethane to CH_3 radicals and N_2 can be readily explained by bond strength arguments. Typically, N=N and C–H bond energies are about 98 kcal/mol each,[19] whereas the C–N bond energy in azomethane is only ~56 kcal/mol.[17] It is clear that significant activation of the N=N bond and the C–H bond must occur on Pd(111) if these two strong bonds are to rupture. If one uses the Redhead equation, assuming a first-order process with $\nu = 10^{13}$ s^{-1}, the activation energy required to break the N–N bond, judging from a dissociation temperature of ~250 K, is only about 16 kcal/mol. For the C–H bond dissociation, judging from the temperature of ~280 K, we estimate an activation energy of only ~19 kcal/mol. Since the C–N bond does not break on Pd(111),[20,21] it must be concluded that its activation energy for bond scission on Pd(111) is significantly higher than the 30 kcal/mol required to desorb the most tightly bound C–N species present (β-HCN). The low bond dissociation energy of N–N can be explained by bonding through its π-bond to the Pd atoms. Similarly, the weak C–H bond can be explained by interaction of the C atom in the CH_3N species on the surface, in similar fashion to the behavior of methylamine on Ni(111).[22]

Azomethane Decomposition: Pd(111) vs Pt(111). The thermal decomposition of azomethane on Pd(111) is similar in several ways to that observed previously on Pt(111).[3] On both surfaces, molecular azomethane, H_2, and HCN are the major desorption products. However, small quantities of CH_4, N_2, C_2N_2, and CH_3NH_2 were also observed to desorb from Pt(111), indicating an activation of the C–N bond on Pt(111) which is absent with Pd(111).

Summary

1. Azomethane adsorbs on the Pd(111) surface molecularly and does not decompose until ~250 K. It is proposed that CH_3N(a) surface species are formed. The final decomposition products liberated as gas-phase species are H_2 and HCN. Thus, C–N bond scission does not occur.
2. Azomethane bonds through nitrogen to the Pd(111) surface.
3. $\Delta\phi$ changes by −1.2 eV with respect to the clean surface upon adsorption of a multilayer coverage of azomethane.
4. There is no observable adsorbate ordering on the surface.

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