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Adsorption, decomposition and isomerization of methyl isocyanide and acetonitrile on Pd(111)

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Abstract

The adsorption of methyl isocyanide (CH_3NC) and acetonitrile (CH_3CN) has been studied on Pd(111). Methyl isocyanide adsorbs on Pd(111) at 80 K at low coverages with the isocyanide functionality oriented close to parallel to the surface; the surface-bound species reorients to a geometry in which the isocyanide group is perpendicular to the surface as the coverage increases. Desorbing the excess isocyanide recovers the parallel geometry. Heating to above $\sim$300 K forms a third, thermally stable, rehybridized species with its $C=N$ axis close to perpendicular to the surface. This thermally decomposes to desorb HCN and hydrogen at above 450 K. Acetonitrile is much less reactive and adsorbs in an $\eta^2(C,N)$ configuration where the adsorbate appears to maintain a reasonably linear $C-C\equiv N$ geometry on the surface and which desorbs with no thermal decomposition at 225 K. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Isocyanides have been studied on transition-metal surfaces since they are isoelectronic with perhaps the most studied adsorbate, carbon monoxide. While CO generally bonds on Group VIII metals via a synergistic bonding scheme with both donation from the metal into empty $2\pi^*$ orbitals on CO and donation from the filled 6σ orbital of CO to the metal [1], methyl isocyanide is a significantly weaker π-acid since its $2\pi^*$ level lies much higher in energy than that of CO [2]. It is therefore interesting from a fundamental point of view, to compare the surface chemistry of these molecules. The isomer of methyl isocyanide, acetonitrile, is also significantly more thermodynamically stable than methyl isocyanide, with an isomerization energy of $\sim$173 kJ/mol, so that it is of interest to probe the way in which this difference in energy affects the surface chemistry [3]. Finally, and perhaps of greatest interest, is the fact that polymeric systems designed to behave as molecular wires have been fabricated using aryl isocyanides in which π-conjugation is maintained throughout the whole molecule [4,5]. The free isocyanide ligands can potentially be attached to the surface so that the π-conjugation is maintained at the surface. This offers the possibility of synthesizing molecular-level conductors that are in electrical contact with the surface at the microscopic level. Understanding the way in which isocyanides bond to the surface is therefore crucial to realizing this potential.

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Isocyanide adsorption has been studied previously on various metal surfaces. On Pt(111) [6–8], CH_3CN was found to adsorb weakly to the surface in a parallel structure (through both the terminal carbon and the nitrogen), and CH_3NC was found to bond strongly in an upright structure with the terminal carbon bonded to two metal atoms. Acetonitrile (methyl cyanide) was investigated further on Pt(111) [9] and again found to adsorb parallel to the surface with a possible interaction between the β-hydrogens and the surface. On supported Pt/SiO_3 [10], similar results were found for both compounds. On powdered Au [11,12], isocyanides were bound weakly to the metal in a linear structure with the terminal carbon bonded to one metal atom. Isocyanides were found to adsorb strongly on Ni(111) and Ni(100) [13–15] in a parallel structure. On Rh(111) [16], the isocyanide bonds strongly also in a parallel structure at low coverages, but converts to a vertical structure at higher coverages. On supported Rh/Al_2O_3 [17], again the isocyanide was found to stand up. Finally, on Ag(311) [18], isocyanides bond weakly in a parallel or close to parallel orientation.

2. Experimental

Experiments were carried out in two stainless-steel, ultra-high vacuum chambers operating at base pressures of 1×10^{-10} Torr following bakeout, and which have been described in detail elsewhere [19,20]. Infrared data were collected from a palladium single crystal sample mounted in a modified $2\frac{3}{4}''$ six-way cross equipped with infrared-transparent, KBr windows. The sample could be resistively heated to 2000 K or cooled to 80 K using liquid nitrogen. Light from a Midac model M2000 infrared spectrometer passes through a polarizer and is focused on the sample at an incidence angle of $\sim 80°$, and the reflected light steered onto the detector of a liquid nitrogen-cooled, mercury cadmium telluride detector. The complete light path is enclosed and purged with dry, CO_2-free air. The spectrometer is controlled using SpectraCalc software and typically operated at $4\,cm^{-1}$ resolution. Data were typically collected for 1000 scans.

In the second chamber, the sample was mounted on a carousel-geometry manipulator and could similarly be resistively heated to 2000 K and cooled to 80 K by thermal contact with a liquid nitrogen-filled reservoir. Temperature programmed desorption (TPD) data were generally collected using a heating rate of $\sim 10\,K/s$, and desorbing species detected using a Dycor quadrupole mass spectrometer interfaced to a PC allowing five masses to be monitored sequentially during the same desorption sweep. In some cases, however, a faster heating rate of $20\,K/s$ was employed to detect species desorbing at higher temperatures. The sample was dosed via a tube which minimized background contamination and dosing of the supports. This gave a pressure enhancement compared with the background pressure of ~ 58 [21]. In order to further minimize spurious signals, the mass spectrometer is enclosed in a shroud with a 1 cm diameter hole in the front.

The sample is cleaned using a standard procedure which consists of heating at 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and then annealing at 1200 K in vacuo to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is not particularly sensitive to the presence of small amounts of carbon on the surface. It was found that a more sensitive gauge of carbon coverage was to saturate the surface with oxygen and perform a TPD experiment. The presence of surface carbon is manifest by the desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly in intensity. The complete absence of carbon is indicated by the desorption of only O_2.

Methyl isocyanide was prepared using literature methods from N-methylformamide (Aldrich, 99%) [22]. Acetonitrile (Aldrich, 99%) was distilled over phosphorus pentoxide. The compounds were transferred to glass vials and further purified by repeated freeze–pump–thaw cycles, and their cleanliness monitored mass spectroscopically.

3. Results

Fig. 1 displays the infrared spectra collected following the adsorption of 3.8 L (1 L = 1 ×
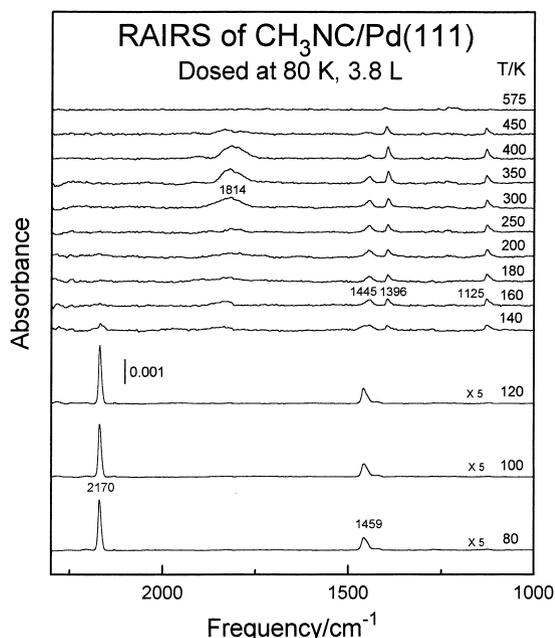
Fig. 1. Reflection absorption infrared spectra (RAIRS) of 3.8 L methyl isocyanide adsorbed on Pd(111) at 80 K and annealed to various temperatures displayed between 1000 and 2300 cm^{-1}. The annealing temperature is marked adjacent to each spectrum.

Table 1
Frequencies and assignments of the RAIR spectrum collected by dosing Pd(111) with 3.8 L of methyl isocyanide at 80 K (species 1) (see Fig. 1)

CH$_3$NC gas-phase frequency (cm^{-1}) [23]	Assignment C$_{3v}$ symmetry	Frequency of CH$_3$NC/Pd(111) (cm^{-1})
2166	$\nu(C\equiv N)$ (a$_1$)	2170
1467	$\delta(CH_3)$ (e)	–
1429	$\delta(CH_3)$ (a$_1$)	1459
1129	$\rho(CH_3)$ (e)	–
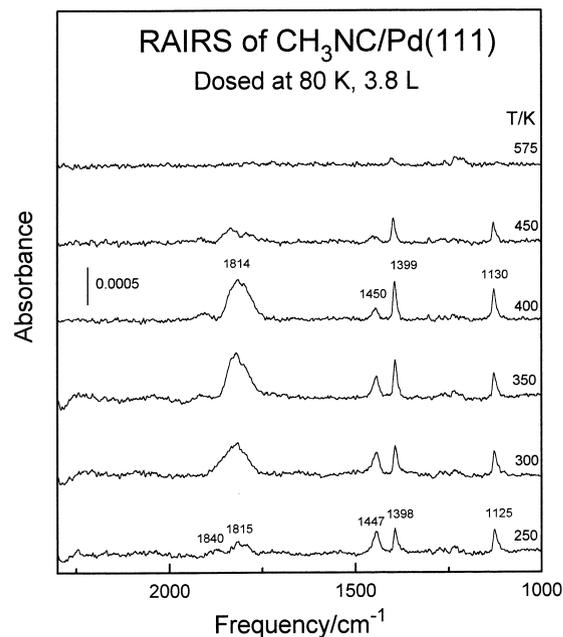
Fig. 2. Expanded RAIRS of methyl isocyanide adsorbed on Pd(111) at 80 K (3.8 L) and annealed to various temperatures following desorption of the multilayer. The annealing temperature is marked adjacent to each spectrum.

10^{-6} Torr s) of methyl isocyanide on Pd(111) at 80 K and shows the effect of annealing the sample to various temperatures. Exposures were not corrected for ionization gauge sensitivities. In these experiments, the sample was heated to the indicated temperature for a period of 5 s in vacuo and then allowed to cool to 80 K following which the spectrum was collected. Note that the spectra collected at 80, 100 and 120 K have been scaled by a factor of five compared with the others. These spectra are essentially identical and exhibit features at 2170 and 1459 cm^{-1}. The spectral assignments are shown in Table 1 and the frequencies of the adsorbed species compared with the gas-phase values. These frequencies are close to the gas-phase values, except that the methyl bending mode increases slightly in frequency. This will be discussed in greater detail below. As the sample is heated to above 120 K, the spectrum changes considerably and now displays significantly more peaks. These spectra are displayed with an expanded absorbance scale in Fig. 2 and show

broad features at $\sim$1815 and 1840 cm^{-1} and sharp modes at 1447, 1398 and 1125 cm^{-1} for sample temperatures of 250 and 300 K. The 1815 cm^{-1} mode increases in intensity as the temperature increases, and the frequencies of the other modes shift slightly to 1450, 1399 and 1130 cm^{-1}. The relative intensities of these features are completely different from those for spectra collected at lower temperatures and, in particular, the $\delta(CH_3)$ mode at 1445 and the $\rho(CH_3)$ mode at 1125 cm^{-1} are

completely absent below 140 K. In addition, the isocyanide stretching mode is at a significantly lower frequency than found for the low-temperature spectra, indicating that these bonds are weakened on adsorption.

Fig. 3 displays a series of spectra collected by sequentially exposing the Pd(111) surface to increasing amounts of methyl isocyanide at 80 K, exhibiting peaks at 1125, 1398, 1447 and 1842 cm^{-1} at exposures of 0.5 and 0.9 L. As the exposure increases to 0.9 L and above, the 1840 cm^{-1} feature decreases in intensity and is replaced by a sharp peak at 2170 cm^{-1}. The 2170 and 1459 cm^{-1} features grow with increasing coverage. This species predominates at even higher exposures, as indicated by the data in Fig. 1. These results indicate that there are two species present on the surface. Species 1, the frequencies of which are shown in Table 1, appears at high coverages for temperatures between 80 and 120 K. Species 2 is present at low coverages, exhibiting peaks at 1840, 1447, 1398 and 1125 cm^{-1}. Removal of methyl isocyanide from a high-coverage surface by

annealing to above 120 K (Fig. 1) restores species 2 (Fig. 2). A similar interconversion between two species as a function of coverage has been observed previously on Rh(111) [16]. The frequencies of species 2 are summarized in Table 2 and assigned by comparison with the gas-phase frequencies [23].

As the sample is heated further, the data of Fig. 2 show that the 1814 cm^{-1} feature increases in intensity. Such a change in intensity indicates that the molecular orientation is changing. The intensity ratio of the 1447 and 1398 cm^{-1} features also varies, with the 1398 cm^{-1} mode increasing in intensity relative to that at 1447 cm^{-1}. In addition, the 1447 cm^{-1} peak shifts slightly to 1450 cm^{-1}. The frequencies and corresponding assignments of this species (designated species 3) are shown in Table 3. The nature of these various surface species will be discussed below. Finally, the 1814 cm^{-1} feature decreases in intensity once again as the sample is heated to 450 K, and the features are essentially absent on warming to 575 K. All that remains at this temperature are broad peaks at 1200 and 1398 cm^{-1}, and these
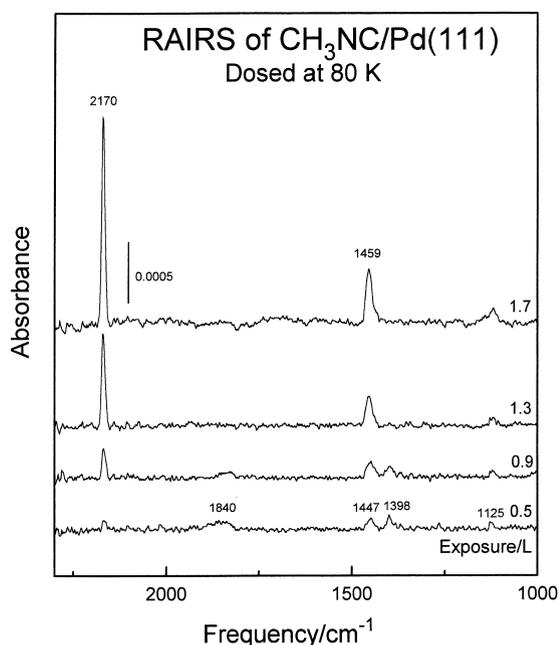
Fig. 3. RAIRS of methyl isocyanide adsorbed on Pd(111) at 80 K as a function of exposure. The methyl isocyanide exposures are marked adjacent to each spectrum.

Table 2
Frequencies and assignments of the RAIR spectrum collected by dosing Pd(111) with 3.8 L of methyl isocyanide at 80 K and heating to above 120 K (species 2) (see Fig. 2)

CH$_3$NC gas-phase frequency (cm^{-1}) [23]	Assignment C$_{3v}$ symmetry	Frequency of CH$_3$NC/Pd(111) (cm^{-1})
2166	ν(C≡N) (a$_1$)	1840
1467	δ(CH$_3$) (e)	1447
1429	δ(CH$_3$) (a$_1$)	1398
1129	ρ(CH$_3$) (e)	1125

Table 3
Frequencies and assignments of the RAIR spectrum collected by dosing Pd(111) with 3.8 L of methyl isocyanide at 80 K and heating to above 300 K (species 3) (see Fig. 2)

CH$_3$NC gas-phase frequency (cm^{-1}) [23]	Assignment C$_{3v}$ symmetry	Frequency of CH$_3$NC/Pd(111) (cm^{-1})
2166	ν(C≡N) (a$_1$)	1814
1467	δ(CH$_3$) (e)	1450
1429	δ(CH$_3$) (a$_1$)	1399
1129	ρ(CH$_3$) (e)	1130

Fig. 4. RAIRS of acetonitrile adsorbed on Pd(111) at 80 K as a function of exposure displayed between 1000 and 2300 cm^{-1}. Exposures are marked adjacent to each spectrum.

finally disappear completely on heating to 650 K (not shown).

The infrared spectra of acetonitrile adsorbed on Pd(111) at 80 K are shown in Fig. 4 as a function of exposure. The spectrum after a 4.0 L exposure displays features at 1040, 1371, 1410, 1447 and 2249 cm^{-1}. The peaks are compared with gas-phase acetonitrile [23] in Table 4 and this indicates that acetonitrile adsorbs molecularly on Pd(111) at 80 K. These features disappear on heating to ~160 K. Based on TPD data (see below), these

Table 4
Frequencies and assignments of the RAIR spectrum collected by dosing Pd(111) with 4.0 L of acetonitrile at 80 K and heating to above 250 K (see Fig. 7)

CH$_3$NC gas-phase frequency (cm^{-1}) [23]	Assignment C$_{3v}$ symmetry	Frequency of CH$_3$NC/Pd(111) (cm^{-1})
2267	ν(C≡N) (a$_1$)	2249
1448	δ(CH$_3$) (e)	1447, 1410
1385	δ(CH$_3$) (a$_1$)	1371
1041	ρ(CH$_3$) (e)	1040

are assigned to acetonitrile adsorbed in second and subsequent layers. Additional features are evident at an exposure of 3.0 L, although multilayer adsorption has clearly commenced prior to the completion of the chemisorbed overlayer. These are assigned to acetonitrile adsorbed in the monolayer and exhibit a broad feature at 1756 with additional sharper peaks at 1304 and 1273 cm^{-1}.

The corresponding TPD spectra are displayed in Figs. 5–7. Fig. 5 displays the 41 amu TPD spectra for acetonitrile (CH$_3$CN) adsorbed on Pd(111) at 80 K. This mass corresponds to the desorption of molecular acetonitrile, and this assignment is confirmed by comparing the yield at various masses with the corresponding mass spectrometer ionizer fragmentation pattern. No other desorption products are detected. It is evident that the monolayer desorbs in a single state centered at 225 K. At higher exposures, a feature appears at 140 K which is assigned to the desorption of acetonitrile multilayers since it continues to grow
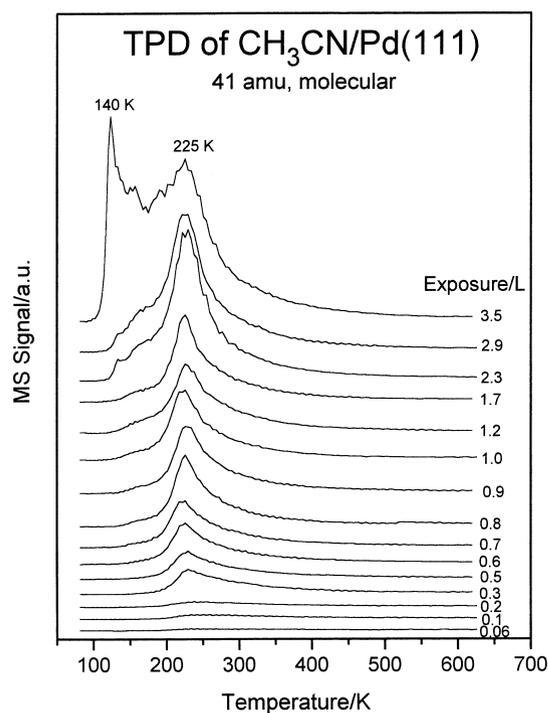
Fig. 5. TPD spectra collected at 41 amu (CH$_3$CN) as a function of acetonitrile exposure using a heating rate of 10 K/s. Exposures are marked adjacent to the corresponding spectrum.
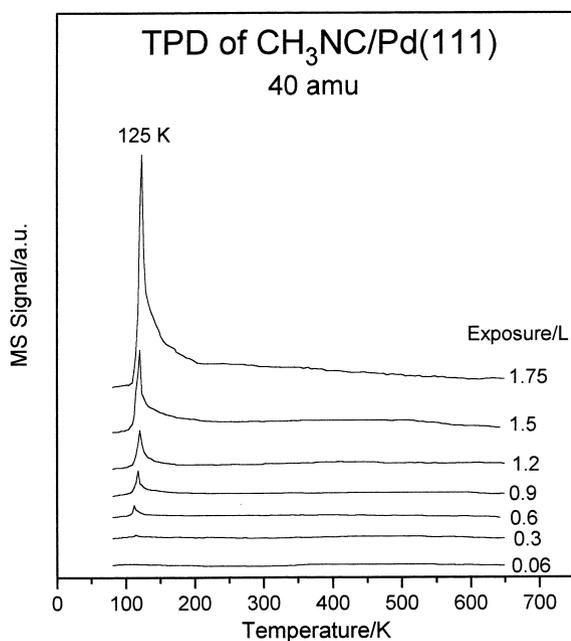
Fig. 6. TPD spectra collected at 40 amu (CH$_3$NC or CH$_3$CN) as a function of methyl isocyanide exposure using a heating rate of 10 K/s. Exposures are marked adjacent to the corresponding spectrum.

Fig. 7. TPD spectra collected at 26 amu (HCN) as a function of methyl isocyanide exposure using a heating rate of 20 K/s. Exposures are marked adjacent to the corresponding spectrum.

with increasing exposure without saturating. The features displayed in Table 4 are assigned to the presence of second and subsequent acetonitrile layers. The appearance of all modes irrespective of symmetry supports this view. The species with frequencies at 1756, 1304 and 1273 cm^{-1} are thus assigned to acetonitrile adsorbed on the Pd(111) surface.

We turn our attention now to the desorption spectra of methyl isocyanide (CH$_3$NC). The 40 amu TPD spectra taken with a heating rate of 10 K/s collected following adsorption of methyl isocyanide on Pd(111) are displayed in Fig. 6. This displays a sharp feature at ∼125 K. The desorption of this species corresponds to the infrared spectral changes observed on annealing the surface to 140 K (Fig. 1). In spite of the relatively low desorption temperature, this species is not assigned to the multilayer, since it appears at relatively low exposures and only modes of a$_1$ symmetry are detected in the infrared spectrum (Table 1), while

all modes would be visible in a randomly oriented multilayer.

The corresponding 26 amu TPD spectra, now taken with a heating rate of 20 K/s, are displayed in Fig. 7 and show an intense peak at 495 K. Measuring the desorption spectrum at other masses shows that this is due to HCN desorption. The peak at 125 K is due to the fragmentation of methyl isocyanide in the mass spectrometer ionizer. Hydrogen desorption is also detected at 495 K, coincident with HCN formation.

4. Discussion

Two distinct methyl isocyanide species are formed depending on coverage in the temperature range 80 to 120 K, which are designated species 1 (Table 1) and 2 (Table 2). Species 2 is formed at low coverages but converts into species 1 as the exposure increases (Fig. 3). It is reformed when the excess methyl isocyanide desorbs on annealing to 140 K (Fig. 1), corresponding to isocyanide

desorption at 125 K (Figs. 6 and 7), emphasizing that the interconversion between these species is reversible. We turn our attention initially to identifying the nature of species 1 (Table 1), which exhibits frequencies that are very close to gasphase methyl isocyanide [23]. Adsorbate geometries can, in favorable cases, be elucidated using infrared spectroscopy, since only the totally symmetric vibrational modes (with a_1 symmetry, i.e. with dipole moments oriented perpendicular to the surface) are detected [24]. It is clear from Table 1 that only a_1 modes are detected, and that all of the modes of e symmetry are forbidden, so that the principle C_{3v} symmetry axis of the molecule is oriented normal to the Pd(111) surface. This indicates that this structure of species 1 is:

$$CH_3 - N \equiv C$$
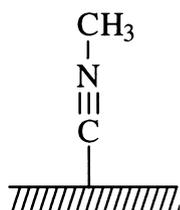
Species 1

where both the $C \equiv N$ and the $C - N$ bonds are oriented perpendicular to the surface. Species 2 (Table 2) has a significantly lower symmetry, since a number of methyl modes that are forbidden in species 1 are detected in species 2. Note, in addition, that the intensity of the 1840 cm^{-1} (isocyanide) mode is very low (Fig. 2). This indicates that the isocyanide functionality is oriented with its axis close to parallel to the surface. The presence of the 1447, 1398 and 1125 cm^{-1} methyl modes further indicates that the carbon—methyl bond is oriented at some intermediate angle to the surface, and the proposed surface structure is depicted below. Species 2 has C_s symmetry and the C_{3v} to C_s correlation table is displayed adjacent to the figure. In this case, the x-axis is perpendicular to the surface, so that all of the vibrational modes now become formally infrared active. The low intensity, however, of the isocyanide stretching mode, as noted above, indicates that this is oriented nearly parallel to the surface, as depicted in the figure. This species interconverts to species 1 as the methyl isocyanide coverage increases, an effect that has been observed previously on Rh(111) [16].
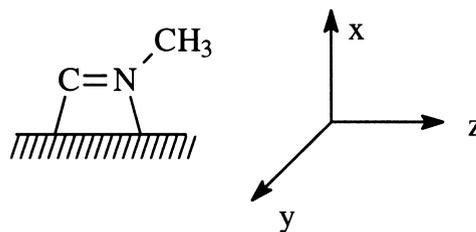
Species 2

C_{3v}	C_s	Symmetry
a_1	a'	x, y
a_2	a''	–
e	$a'+a''$	x, y, z

As the temperature increases to 300 K, a further spectral transformation takes place producing species 3 (Fig. 2; Table 3). Since the intensity of the isocyanide mode at 1814 cm^{-1} increases significantly as this species forms, this suggests that the isocyanide bond becomes oriented more closely with the surface normal and its bond order is significantly reduced. The continued presence of all the modes due to the methyl species implies that the methyl mode is oriented at some intermediate angle with respect to the surface. A proposed structure for species 3 is depicted below:
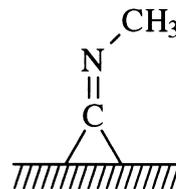
Species 3

The isocyanide bond is depicted as oriented normal to the surface, although the exact orientation is not known.

Species 3 is remarkably stable on the surface and persists up to a surface temperature of above 400 K. Methyl groups adsorbed on Pd(111) thermally decompose to yield carbon and hydrogen at ∼300 K, and the methyl species hydrogenates to methane at 210 K on this surface [25,26]. The

remoteness of the methyl group from the surface in species 3 clearly renders it significantly less labile. This species does, however, begin to thermally decompose at ∼450 K. No methane desorption is detected, so that the methyl group immediately undergoes thermal decomposition. The observation of simultaneous desorption of HCN (Fig. 7) and hydrogen in TPD spectra, coincident with the loss of features due to species 3 (Fig. 2), indicates that this decomposes to yield HCN and H_2, and that this is limited by the rate of decomposition of species 3.

The reaction pathway for methyl isocyanide adsorbed on Pd(111) is summarized in Scheme 1. The chemistry of acetonitrile is significantly simpler, since it adsorbs molecularly on the surface and desorbs as an intact molecule at 225 K (Fig. 5). Assuming that this desorption is a first-order process with a pre-exponential factor of 1.0×10^{13} s^{-1}, the desorption activation energy is 55 kJ/mol [27]. This is not surprising, since acetonitrile is significantly more stable than methyl isocyanide, where the heat of isomerization is ∼173 kJ/mol [3]. The multilayer desorbs at ∼140 K (Fig. 5), and the monolayer exhibits features at 1755, 1304 and 1273 cm^{-1}. The 1755 cm^{-1} feature is assigned to a C≡N stretching mode that has been softened considerably due to interaction with the surface. The C≡N stretching frequency is similarly softened to ∼1680 cm^{-1} on Pt(111) [9], where it is assigned to the presence of

an $\eta^2(C,N)$ species. The similarly large shift on Pd(111) suggests that a similar species is present, although the mode is softened slightly less on Pd(111) than on Pt(111). Interestingly, the modes associated with the methyl species were only slightly perturbed from their gas-phase values on Pt(111) whereas, assuming that the 1304 and 1273 cm^{-1} modes on Pd(111) are methyl bending modes (Fig. 4), these modes appear to be significantly more strongly perturbed on palladium than platinum. This implies that the methyl modes for acetonitrile adsorbed on Pd(111) interact with the surface more strongly than on platinum. This suggests that the cyanide carbon is less strongly perturbed on platinum than on palladium, resulting in a more linear C−C≡N bond in the latter case. Certainly the less strongly perturbed C≡N stretching frequency {1755 cm^{-1} on Pd(111) versus 1680 cm^{-1} on Pt(111) [9]} is in accord with this conclusion. Thus, acetonitrile is proposed to adsorb in an $\eta^2(C,N)$ configuration on Pd(111), but with a substantially lower extent of rehybridization than on platinum.

5. Conclusions

Methyl isocyanide adsorbs on Pd(111) at 80 K, where the orientation depends on coverage, with a parallel orientation predominating at low coverages but converting to a perpendicular orientation

Scheme 1.
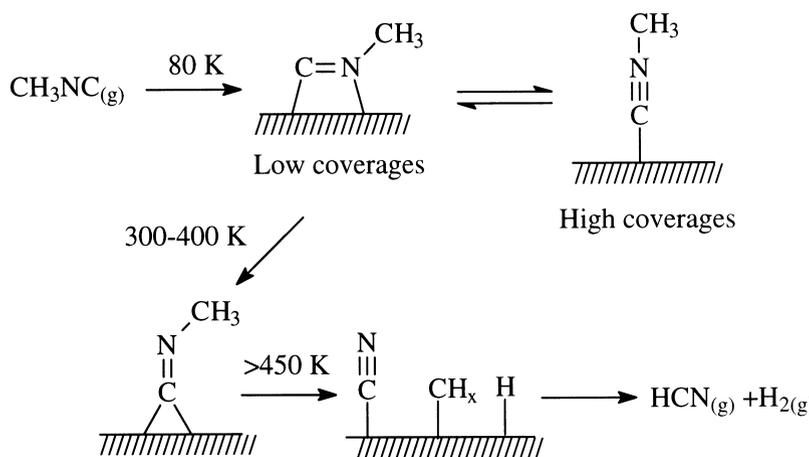
as the coverage increases. On heating to between 300 and 400 K, methyl isocyanide converts to a third species in which the isocyanide bond is oriented perpendicular to the surface, but with the carbon substantially rehybridized. This species thermally decomposes on heating, and the products thermally desorb as HCN at 495 K. In contrast, acetonitrile adsorbs and desorbs molecularly at 255 K and adopts an $\eta^2(C,N)$ configuration, where the acetonitrile appears to maintain a reasonably linear $C-C\equiv N$ bond on the surface.

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