Formation of μ_2,η^2-Diaminoethylene (H_2NCCNH_2) from Cyanogen (C_2N_2) and Hydrogen on Pt(111): Characterization of a Diiminium Surface Species

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The cyclotrimerization of acetylene to benzene[1] and the hydrogenation of nitriles to amines[2] are two important catalytic processes that occur on Group VIII transition metal surfaces. The surface-catalyzed cyclotrimerization of either diamino or dihalogeno-substituted acetylinic or dimetalated olefinic surface intermediates remains uninvestigated, even though a number of clusters containing analogous precursor ligands have been characterized.[3] By using Fourier transform-reflection absorption infrared spectroscopy (FT-RAIRS), we have for the first time identified μ_2,η^2-diaminoethylene, $(CNH_2)_2$, as a stable hydrogenation product of cyanogen (C_2N_2) on Pt(111). The similarities between μ_2,η^2-diaminoethylene and the previously identified aminomethylidyne (CNH_2) species[4] show that a new class of surface intermediates containing iminium- ($C{=}NH_2$) like functionalities are formed by hydrogenation of C_2N_2 and CN on Pt(111). Iminium intermediates appear to play an important role in the hydrogenation/dehydrogenation chemistry of CN-containing species on Group VIII transition metal surfaces, as aminomethylidyne has also been observed during the thermal decomposition of hydrogen cyanide (HCN), azomethane ($CH_3N_2CH_3$), and methylamine (CH_3NH_2).[4,5]

The chemistry of cyanogen on platinum and other transition metal surfaces has been investigated using a variety of experimental techniques.[6−8] It has been shown that cyanogen adsorbs either molecularly at low temperature or dissociatively at higher temperatures, forming the α C_2N_2 state or β CN states, respectively.[6] It has been proposed that cyanogen can also adsorb dissociatively below 368 K on Pt(111), simultaneously forming both the α and β states,[6] but experimental verification of this hypothesis has proven difficult.[8] The hydrogenation product of C_2N_2 that forms on Pt(111) has been studied previously with TDS,[6] HREELS,[7] and XPS.[8] The resulting species was found to be stable in the range of 250−430 K, giving rise to bands at 3350, 1560, and 1450 cm^{-1}. These HREELS bands, which are essentially identical in frequency to the higher resolution RAIRS bands we observe, were interpreted as the respective ν(NH), ν(CN), and δ(HNC) modes of a $HN{=}CH{-}CH{=}NH$ diimine species. The assignment of the observed spectra to the above 1,2-diiminoethane species is qualitatively correct in terms of a comparison with established imine group frequencies. Verification of these assignments via a series of ^{15}N and ^{13}C isotopic substitution requires a greater resolution than is typically available with HREELS, although experiments of this nature are possible using RAIRS.

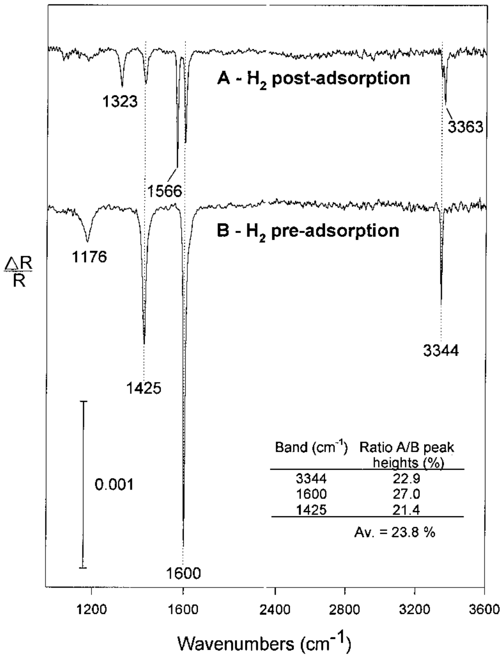

Figure 1. Coadsorption of 0.25 L of cyanogen (C_2N_2) and 10 L of hydrogen. If hydrogen is preadsorbed, diaminoethylene $(CNH_2)_2$ is formed exclusively (B). The postadsorption of H_2 results in the formation of both aminomethylidyne (CNH_2) and diaminoethylene (A). Both spectra were acquired using an MCT detector.

All the experiments discussed below were carried out in a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 5 \times 10^{-11}$ Torr. A detailed description of this system can be found elsewhere.[9] All RAIR spectra were recorded at 300 K using 2048 coadded scans with a resolution of 4 cm^{-1}. An MCT (HgCdTe) detector was used to obtain spectra between 4000 and 800 cm^{-1}, while an InSb detector with a low wavenumber cutoff of 1900 cm^{-1} was used to obtain complementary spectra above 1950 cm^{-1}. The cyanogen isotopomers used were in each case prepared via the thermal decomposition of the appropriate AgCN salt. $Ag^{12}C^{14}N$ (99%) was obtained directly from Aldrich Chemical Co., while $Ag^{13}C^{14}N$ and $Ag^{12}C^{15}N$ were synthesized by reacting $AgNO_3$ (aq) with solutions of $K^{13}C^{14}N$ (99%) and $K^{12}C^{15}N$ (98+%). Both potassium cyanide salts were obtained from Cambridge Isotope Laboratories. Each cyanogen isotopomer, once prepared, was further purified by performing several freeze−pump−thaw cycles.

In Figure 1 the RAIR spectra obtained by coadsorbing 0.25 L (1 L = 1×10^{-6} Torr s) of C_2N_2 and 10 L of H_2 on a clean Pt(111) surface are displayed. The order in which these two gases are dosed has important consequences for the resulting spectra, A and B. The postadsorption of H_2 produces spectrum A, which contains six bands. The bands observed at 1323, 1566, and 3363 cm^{-1} are due to the respective ν(CN), $\delta(NH_2)$, and $\nu(NH)_{sym}$ modes of aminomethylidyne[4] (CNH_2), which is formed by the hydrogenation of CN. The presence of CN indicates that cyanogen undergoes partial dissociative adsorption on Pt(111) at 300 K. Three other bands due to a second coadsorbed species are also observed in spectrum A at 1425, 1600, and 3344 cm^{-1}. These bands are due to the respective ν(CN), $\delta(NH_2)$, and $\nu(NH)_{sym}$ modes of diaminoethylene, $(CNH_2)_{2ads}$, which is formed by the hydrogenation of C_2N_2. The characterization of this new species was accomplished by the

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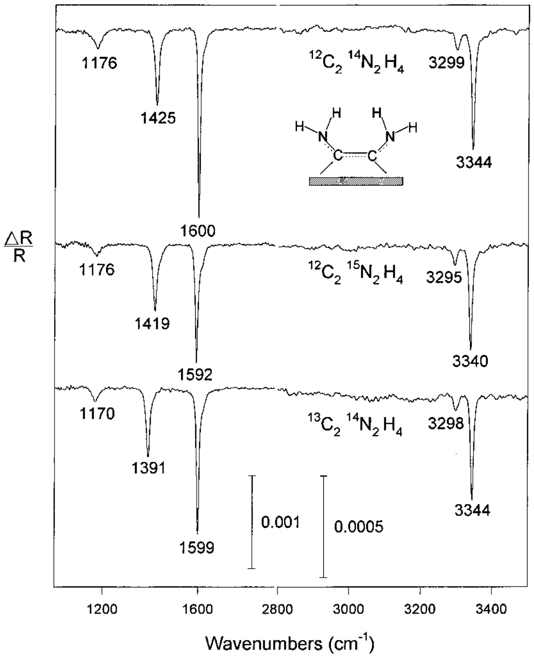

Figure 2. Spectra of the diaminoethylene isotopomers formed after coadsorbing 10 L of H_2 with 0.25 L each of $^{12}C_2{}^{14}N_2$,$^{12}C_2{}^{15}N_2$, and $^{13}C_2{}^{14}N_2$, respectively. The relative isotopic shifts show that the hydrogenated cyanogen species is diaminoethylene, $(CNH_2)_2$. Spectra below 1950 cm^{-1} were acquired using an MCT detector, while an InSb detector was used to obtain complementary spectra above 1950 cm^{-1}.

use of ^{15}N and ^{13}C isotopic substitution experiments, which are discussed in detail below. The preadsorption of H_2 (spectrum B) results in the exclusive formation of the new $(CNH_2)_2$ species. The band that appears at 1176 cm^{-1} in B, which is too weak to be observed in A, is assigned to the ν(CC) mode of diaminoethylene. The preadsorption of H_2 apparently inhibits the dissociative adsorption of cyanogen to CN, as only the hydrogenation product of C_2N_2 (diaminoethylene) is observed in B. If the individual peak heights of the 1425, 1600, and 3344 cm^{-1} bands of diaminoethylene in A and B are compared, then an average A/B peak height ratio of 23.8 ± 3.2% for the three pairs of bands is obtained. This result suggests that the bands assigned to diaminoethylene are in fact due to a single species, as the relative intensities of these bands only vary by ±3.2% for different coverages. If it is assumed that all of the C_2N_2 becomes hydrogenated to form $(CNH_2)_2$ in both A and B, then it is estimated (on the basis of relative peak heights) that ~23.8% of the original 0.25 L of C_2N_2 dosed at 300 K adsorbs molecularly while the remainder adsorbs dissociatively as CN_{ads}.

In Figure 2 the RAIR spectra obtained after coadsorbing 10 L of H_2 with 0.25 L each of $^{12}C_2{}^{14}N_2$, $^{12}C_2{}^{15}N_2$, and $^{13}C_2{}^{14}N_2$ on a clean Pt(111) surface are displayed. In each case H_2 was predosed in order to selectively form the relevant diaminoethylene isotopomer. The relative isotopic shifts observed for the bands of $(^{12}C^{14}NH_2)_2$ under ^{15}N and ^{13}C substitution are shown in Table 1. The isotopic shifts of the ^{15}N and ^{13}C isotopomers' bands with respect to those of $(^{12}C^{14}NH_2)_2$ allow for definitive mode assignments. The two high-frequency bands at 3344 and 3299 cm^{-1} are both red shifted by four wavenumbers with ^{15}N substitution but remain virtually unaffected by ^{13}C substitution. This clearly shows that these bands are due to ν(NH) modes. The 1600 cm^{-1} band is strongly shifted by ^{15}N substitution, but is negligibly affected by ^{13}C substitution. These observations indicate that this band is due to a $\delta(NH_2)$ mode. The 1425 cm^{-1} band is downshifted by both ^{13}C and ^{15}N substitution, indicating that it is due to a ν(CN) mode. The band at 1176 cm^{-1} is clearly due to a ν(CC) mode since it is downshifted by ^{13}C but unaffected by ^{15}N substitution. It should be noted that the superior sensitivity of the InSb with respect to the MCT detector in the 1950−4000 cm^{-1} region allowed for measurement of the various weak NH stretch bands shown in Figure 2 at ~3299 cm^{-1}. These weak bands are not observed in Figure 1, where only the less sensitive MCT detector was used. The observation of two symmetric ν(NH) modes in Figure 2 is consistent with the sym−sym and asym−asym NH stretch combinations of the adsorbate's individual CNH_2 moieties. Both of these allowed modes are totally symmetric with respect to the symmetry operations of the adsorbate, belonging to the A_1 symmetry representation of the C_{2v} point group. The observation of two NH stretches is consistent with the NH_2 groups of diaminoethylene but not with NH groups of a diimine species. The ^{15}N and ^{13}C isotopic shifts of the 1600 and 1425 cm^{-1} bands are also inconsistent with their respective assignments as the ν(CN) and δ(HNC) modes of a 1,2-diiminoethane surface species. The observation of what appears to be a partial C−C double bond at 1176 cm^{-1} is consistent with the highly perturbed ν(CC) mode of numerous acetylinic adsorbates.[10] On Pt(111) the molecular plane of such highly perturbed acetylene- (C_2H_2) derived adsorbates has been shown to be tilted with respect to the surface normal.[11] In contrast, the low number of bands observed here for diaminoethylene implies that the adsorbate has a high degree of symmetry, thereby precluding such a tilted geometry. Furthermore, the frequencies derived from a series of normal mode calculations using a planar C_{2v} model of μ_2,η^2-diaminoethylene, bonded to two Pt atoms with a dimetalated olefinic geometry, were found to be in excellent agreement with the experimental values.[12] The relative isotopic shifts displayed in Table 1 are almost identical to those observed for aminomethylidyne (CNH_2) and its ^{15}N and ^{13}C isotopomers, even though the absolute frequencies of the two species' analogous bands are in some cases separated by upward of 100 cm^{-1}. This alone suggests that both aminomethylidyne and diaminoethylene have similar internal coordinates and share an iminium-like functionality, an interpretation which has also been confirmed by normal mode calculations.[12]

Table 1. Isotopic Shifts and Band Assignments for Diaminoethylene $(CNH_2)_2$ and Aminomethylidyne $(CNH_2)^a$

$(^{12}C^{14}NH_2)_2$ freq (cm^{-1})	^{15}N $\Delta\nu$ (cm^{-1})	^{13}C $\Delta\nu$ (cm^{-1})	mode
3344 (3363)	−4 (−4)	0 (0)	$\nu(NH)_s$
3299 (3363)	−4 (−4)	−1 (0)	$\nu(NH)_s$
1600 (1566)	−8 (−8)	−1 (−1)	$\delta(NH_2)$
1425 (1323)	−6 (−11)	−34 (−33)	ν(CN)
1176 (−)	0 (−)	−6 (−)	ν(CC)

[a] Values in parentheses are for aminomethylidyne (CNH_2).

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