Totally Selective NN Bond Cleavage in the Dissociative Adsorption of Diazirine on Cu(110)

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Abstract: CN versus NN bond cleavage selectivity in the chemisorption of diazirine on Cu(110) and copper films was studied using temperature-programmed desorption and X-ray photoelectron spectroscopy. Dissociative adsorption occurs at or below 124 K, yielding XPS spectra characteristic of atomic nitrogen and species containing CN bonds. The TPD spectra show that the decomposition products rearrange or recombine, leading to high-temperature N_2 and C_2N_2 desorption. In combination, these results show that dissociative adsorption of diazirine on Cu(110) involves totally selective NN bond scission. Results for the adsorption of diazirine on copper films deposited at 107 K also show that dissociative adsorption occurs through selective NN bond scission. Furthermore, the fact that similar dissociation chemistry is observed for both the atomically rough films and the single-crystal surface implies that the selective NN bond scission should be interpreted in terms of electronic structure. The selective chemistry on copper is interpreted with reference to previous results for Pd(110), where both CN and NN bond scission were observed. An analysis based on the match between the molecular frontier orbitals and the metal valence band structure suggests that the π-σ bonding interactions in the chemisorption of diazirine are antisynergistic. The observed surface decomposition of diazirine is compared to data from the organometallic literature for the interaction of diazirine compounds with metal complexes.

1. Introduction

Diazirine **1**, Figure 1, is a cyclic isomer of diazomethane and is the simplest member of the family of diazirines. Gas phase thermolysis and UV photolysis of diazirine yields N_2 and the :CH_2 diradical.[1−5] Hence, it may be considered as a potential methylene generating molecule for surface studies related to hydrocarbon synthesis and transformation. However, as outlined below, the organometallic literature shows that bond scission of both CN and NN can occur when diazirines interact with metal complexes. The formation of carbene ligands arises from a selective cleavage of the CN bonds.[6−9] On the contrary, selective NN bond scission results in the formation of alkylideneimino (R_2CN) ligands.[10−12] This paper focuses on the selectivity of copper surfaces with respect to CN and NN bond scission in the dissociative adsorption of diazirine.

The organometallic chemistry of diazirines has been studied in some detail.[6−12] Chaloner et al.[6−8] used aryl (methoxy) diazirines to synthesize terminal and bridging metal carbene complexes. Their work shows that insertion of $Cr(CO)_5THF$ and $W(CO)_5THF$ complexes into diazirine CN bonds leads to the formation of terminal carbenes **2** and the elimination of molecular nitrogen.[6] In a more recent study, the same group showed that the reaction of aryl (methoxy) diazirines with $[M_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ (M=Rh or Co) forms μ-carbene complexes **3** through the concerted addition of free carbene to the metal−metal double bond.[8] This conclusion is based on the fact that no reaction was observed below the thermal decomposition temperature of the diazirine compound. Organometallic chemistry involving the selective cleavage of the NN bond is outlined in reviews by Kisch et al.[10,11] For example, alkylidenimino and isocyanate complexes **4** are detected as minor products in the interaction of dimethyldiazirine with $Fe_2(CO)_9$ in THF.[12]

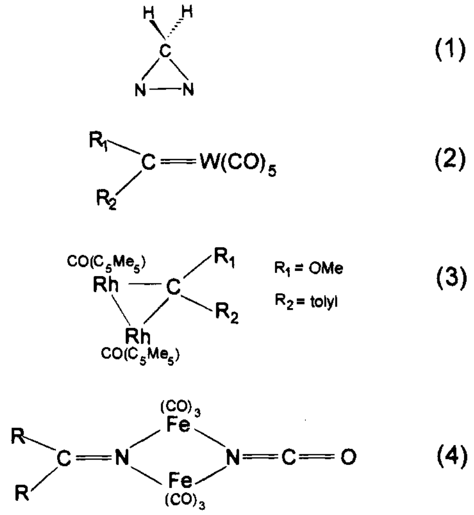

Figure 1. Illustration of the molecular structure of diazirine, CH_2N_2, and of various metal complexes prepared using substituted diazirine, CR_2N_2, compounds.[6−12]

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The basic experimental approach underlying our study is quite similar to the methodology for the controlled synthesis of carbene complexes developed by Doye et al.[9] The latter group exploited the fact that diazirines are relatively inert compared to linear diazoalkane reagents. Hence, they found that they could securely introduce a diazirine compound into the reaction milieu and then activate the carbene synthesis in situ using UV irradiation. Similarly, in the case of studies in stainless steel UHV chambers, diazirine is much less likely to decompose on the chamber walls than is the more reactive diazomethane. Hence, diazirine can be delivered intact to the metal surface under study. The chemisorption interaction with the clean surface then activates the molecule, leading to possible dissociation.

Since diazirine is a relatively complex and little-studied adsorbate, it is useful to compare its frontier orbitals to those of the well-studied CO adsorbate. As detailed in the discussion, such a comparison reveals that diazirine resembles carbon monoxide in that it has a relatively low-lying unoccupied π^* level and a HOMO orbital which lies close in energy to the 5 σ HOMO orbital of CO.[13] Hence, it may be profitable to treat the chemisorption of diazirine in terms of the donor−acceptor bonding model often used to describe the chemisorption of CO on metals. Nevertheless, diazirine is obviously a much more complex molecule than CO. Apart from the fact that it is polyatomic, it is also cyclic and possesses a strain energy of approximately 20 kcal/mol.[14]

Previous work on the adsorption of diazirine on Pd(110) has shown that this molecule is a sensitive probe of the chemisorption bond.[15] Two different types of adsorption geometry were observed on Pd(110), one in which the NN bond of diazirine was roughly parallel to the surface and one in which the NN bond was tilted away from the surface. The latter geometry principally involved a σ-donor interaction with the surface, whereas the former geometry permitted additional strong π-overlap with metal orbitals. The consequences of these adsorption geometries, in terms of CN and NN bond activation, were discussed in terms of the character of the diazirine frontier orbitals.[15] The HOMO orbital in diazirine is a cyclic orbital which is bonding in CN and antibonding in NN. The π^*, LUMO, orbital is simply antibonding in NN.[1,2] Given the CN bonding and NN antibonding nature of the cyclic HOMO orbital, pure σ-donor chemisorption is expected to weaken the CN bonds and strengthen the NN bond.[1] On the other hand, an adsorption geometry involving π-overlap with the metal is expected to weaken the NN bond,[15] through back-donation into the LUMO orbital. Using the above line of reasoning, the observation of bond scission of both CN and NN on Pd(110) was interpreted in terms of the selective activation of the CN and NN bonds as a function of the adsorption geometry.

The interaction of simple molecules with copper is usually weak compared to that observed for adsorption on transition metals.[16,17] However, we find that diazirine dissociates at even lower temperatures on Cu(110) than on Pd(110). Furthermore, in contrast to the case for diazirine on Pd(110), totally selective NN bond scission occurs on Cu(110). Similarly, diazirine dissociates via NN bond scission on atomically rough films at the lowest temperatures studied, 107 K. An explanation for the greater reactivity and selectivity of copper, as compared to that of palladium, is given in terms of the match of the valence electronic structure of diazirine with that of the two metals. On the basis of this comparison, we suggest that an antisynergistic π-σ bonding interaction[13] is operative in the chemisorption of diazirine on metal surfaces.

2. Experimental Section

Experiments were performed in a stainless steel UHV system with a 2×10^{-10} mbar base pressure. X-ray photoelectron spectra were obtained using a spherical analyzer set at a pass energy of 20 eV and calibrated against the Cu($2p_{3/2}$) peak at 932.4 eV. The acquisition time was 200 s for the C(1s) and N(1s) regions over a 10 eV range. Spectra were fitted, after removal of the Cu background, using a mix of Gaussian and Lorentzian functions. Quantitative information was obtained using the following calibration procedure. The clean Cu(110) surface was exposed to 100 L of O_2 at room temperature, under the assumption that this produces a surface coverage of 0.5. This assumption is based on literature data[18] on the formation, by exposure to 20−1000 L of O_2 at room temperature, of the O/Cu(110)-(2×1) reconstructed phase. The half monolayer O(1s)/Cu($2p_{3/2}$) intensity ratio was then taken as a standard for calculating carbon and nitrogen surface concentrations using the appropriate atomic surface sensitivity factors.[19] Surface concentrations for nitrogen and carbon on the coppper films were calculated using the method described by Carley and Roberts.[20] These quantitative measurements were used to estimate the surface coverages involved in the different experiments. The XPS measurements showed that the uncorrected exposure levels reported in this article are about an order of magnitude lower than the actual values.

TPD spectra were collected at a heating rate of 1 K/s. The Cu(110) crystal (Monocrystals Co.) was mechanically held on a tantalum sheet by small clamps folded into a groove made along the circumference of the crystal. The sample was resistively heated by two tantalum wires spot-welded onto the back of the Ta sheet, and the temperature was monitored using a chromel−alumel thermocouple spot-welded to the tantalum. This method of measuring the temperature of the copper crystal is indirect and introduces some error in the TPD measurements at high temperatures. Sample cleanliness, in the sensitivity limit of XPS, was obtained by repeated cycles of Ar bombardment (3 μA, 500 eV, 450 K) for 15 min and annealing at 940 K for 5 min. Carbon impurities were removed by heating in 1×10^{-7} mbar of oxygen at 600 K followed by annealing. Copper films were evaporated from a resistively heated tungsten basket onto a tantalum foil held at 107 K. Diffusion-limited ballistic film growth at such low temperatures results in atomically rough surfaces.[21] Gross structural changes in the copper films occur during the desorption ramp. These are evidenced, in separate measurements, by an approximately 2-fold decrease in the Cu photoemission intensity above 400 K. The decrease results from surface free energy driven island formation and particle growth. Atomic force microscope images of particle growth on annealing silver films are shown in a recent paper by Van Duyne et al.[22]

Diazirine (CH_2N_2) was prepared according to the modification of the Ohme and Schmitz method[23] described by Gambi et al.,[24] with the exception that the sodium hypobromite solution was cooled in an ice bath before injection over the methylenediamine sulfate salt. The volatile product was purified by passing it through a series of traps immersed in pentane−liquid nitrogen slushes. Particular care should be exercised in handling diazirine as it is a hazardous compound.[15] The mass spectrum measured on introduction of diazirine to the UHV chamber sometimes included a weak signal at 44 amu, possibly due to a CO_2 or diaziridine impurity. Cyanogen was generated by decomposition of AgCN in a gas handling line at 600 K and used without any further purification.

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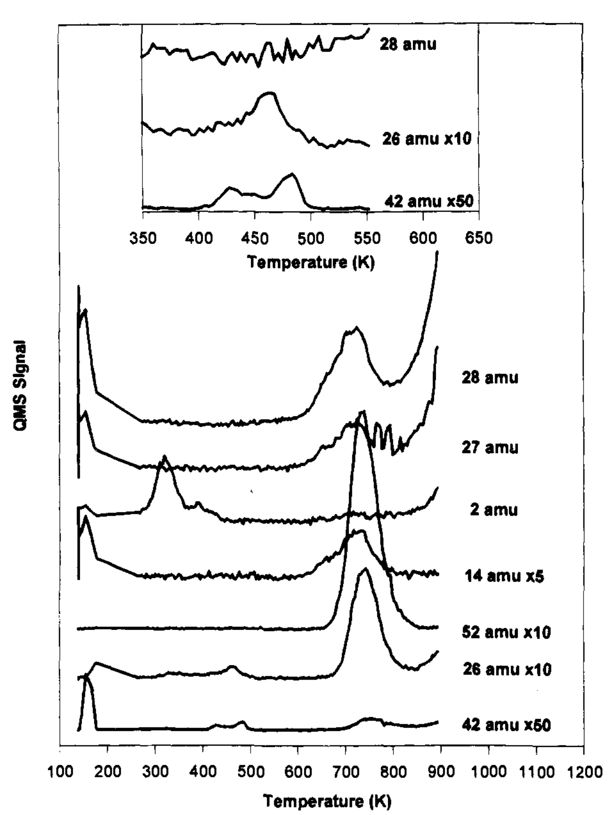

Figure 2. Temperature-programmed desorption spectra obtained following exposure of Cu(110) to 0.15 L of diazirine at 124 K. The insert shows the weak desorption features in the 400–500 K region on a magnified scale.

3. Results

This paper deals with a determination of the initial bond breaking selectivity in the interaction of diazirine with copper. Hence, the results presented herein will be used to differentiate between NN and CN bond scission rather than to determine the exact identity of all surface species.

Thermal-Programmed Desorption Results. The following masses, m/q = 2, 14, 15, 16, 25, 26, 27, 28, 30, 31, 32, 42, 43, 44, 46, 52, 56, and 80, were monitored eight to ten at a time. A thermal desorption spectrum, obtained following exposure to 0.06 L of CH_2N_2 at 124 K, is shown in Figure 2. The sharp features at the start of the temperature ramp are due to desorption from the sample holder. The weak $m/q = 42$ desorption feature at 150 K is due to desorption of a small fraction of molecular diazirine. However, the interaction of diazirine with Cu(110) at 124 K is predominantly dissociative. As shown in Figure 2, there are three major TPD features. A feature comprising 28, 27, and 14 amu peaks appears at $T_{\max} = 700$ K, a feature displaying 52 and 26 amu peaks appears at 760 K, and a H_2 desorption maximum occurs at 330 K. In addition, weak desorption features for masses $m/q = 42$ and 26, but not for $m/q = 28$, occur in the 400–500 K region. The latter desorption features are highlighted in the insert to Figure 2. Note that the traces shown in the insert display different shapes, thereby indicating that more than one species is giving rise to the TPD features in the 400–500 K region. This set of peaks is seen in bigger proportion for atomically rough copper films, which may indicate that they are related to chemistry at defect sites. The desorbing species are possibly isomers of diazirine. However, the spectra do not match those recently published for cyanamide, H_2NCN.[25] Nevertheless, the fact that a $m/q = 28$ peak is not observed indicates that the desorbing species do not contain an NN bond. No desorption features were observed in the region 200–300 K in any of the experiments.

Since the TPD spectra shown in Figure 2 suggest the desorption of C_2N_2 at 760 K, a series of calibration TPD measurements were performed on the interaction of cyanogen with Cu(110). Exposure to cyanogen at 124 K yielded desorption features at 760 K with the same $(m/q = 26)/(m/q = 52)$ intensity ratio as the high-temperature feature in Figure 2. Since, in addition, the ratio of the $m/q = 28$ to $m/q = 14$ peaks at 700 K in Figure 2 is equal to that measured for N_2 in our system, these results confirm the high-temperature desorption of nitrogen and cyanogen.

The desorption temperatures for nitrogen and cyanogen are in good agreement with those reported by Baddorf and Zehner[26] and Outka et al.,[27] respectively. Baddorf and Zehner found that nitrogen atoms recombine on Cu(110) to yield a desorption peak at 730 K. Note that Heskett et al.[28] have shown that the desorption temperature of molecularly adsorbed nitrogen from Cu(110) is approximately 130 K. The hydrogen desorption peak temperature (330 K) matches reported values for recombinative desorption of hydrogen from Cu(110),[29] and this indicates that at least partial dehydrogenation of the dissociation products occurs at lower temperatures. In summary, the TPD data show that N_2, C_2N_2, and H_2 are the major desorption products and that these result from recombination on the surface. The origin of the amss 27 peak which tracks the mass 28 and 14 signals is not clear. Nevertheless, the absence of a mass 26 signal shows that it cannot be attributed to either C_2H_4 or HCN, nor can it be attributed to any simple C_xH_y molecule, which might result from the polymerization of surface methylene species.

XPS Results. C(1s) and N(1s) spectra were recorded as a function of exposure of Cu(110) at 124 K to diazirine. A single C(1s) peak at 285.4 eV grows in intensity and eventually saturates at approximately 0.15 L. The full width at half maximum remains constant at 1.3 eV as a function of coverage. The N(1s) region displays a broad (2.2 eV FWHM) asymmetric peak indicative of signal from two or more surface species. As with the C(1s) intensity, the N(1s) signal saturates at about 0.15 L. Typical N(1s) and C(1s) spectra, taken at 124 K, are shown in the bottom traces of Figure 3. An additional broad N(1s) peak at 402.1 eV is seen for approximately monolayer coverage of diazirine on copper films at 107 K. By reference to previous results[15] for Pd(110), the peak at 402.1 eV is assigned to molecular diazirine. This feature is removed on heating the films to 150 K. The TPD data for diazirine on Cu(110) display a weak molecular desorption peak at 150 K. However, the 402.1 eV peak is not observed in the XPS spectra of Cu(110). Furthermore, annealing the sample from 124 to 200 K does not cause a decrease in the N(1s) signal. These results indicate that the weak molecular desorption feature actually arises from the sample holder or the crystal sides. Thus, in the limit of the sensitivity of our XPS spectrometer, all of the species on the Cu(110) surface at 124 K are the result of the dissociative adsorption of diazirine.

Changes induced in the C(1s) and N(1s) spectra by annealing the sample in the range 124–630 K are shown in Figure 3. All spectra were simulated using a peak synthesis approach. A shift in the C(1s) binding energy from 285.4 to 286.0 eV occurs in the 240–380 K temperature range. In roughly the same tem-

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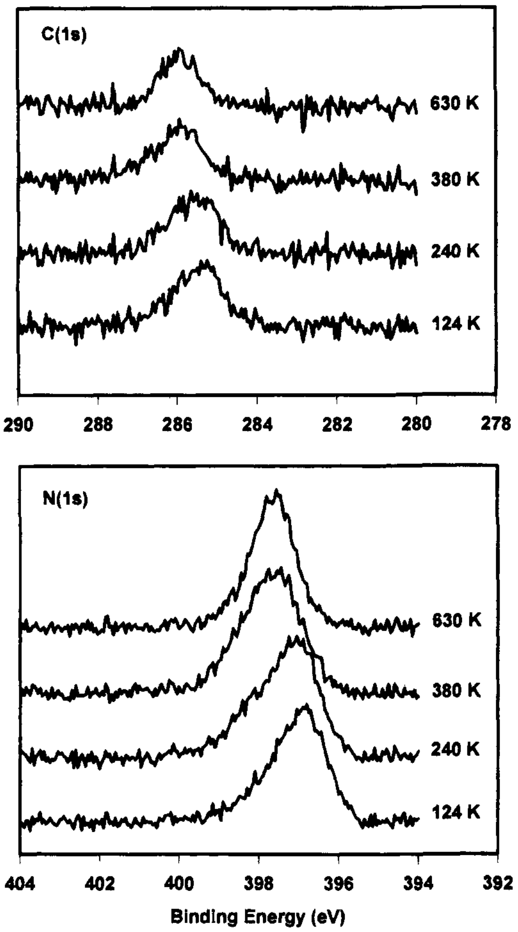

Figure 3. C(1s) and N(1s) spectra as a function of anneal temperature following exposure of Cu(110) to 0.15 L of diazirine at 124 K. The C(1s) and N(1s) signals are completely removed above 800 K.

perature range, the N(1s) peak shifts from 396.8 to 397.7 eV. The C(1s) and, in particular, the N(1s) feature become more symmetric on annealing to 630 K. The shifts in binding energies above 240 K are at least partially due to dehydrogenation, since dehydrogenation is required to produce the hydrogen desorption peak at 330 K. The changes in peak shapes above 380 K are at least partially due to the removal of some surface species in the region 400−500 K, as evidenced by the TPD peaks shown in the inset of Figure 2. However, XPS is not specific enough, as a molecular technique, to identify the chemical transformations which occur in the 124−530 K range. Nevertheless, the XPS and TPD data as shown below are sufficient to infer the bond breaking processes which occur on adsorption. The latter question, formulated in terms of CN and NN bond breaking selectivity, is the focus of this paper.

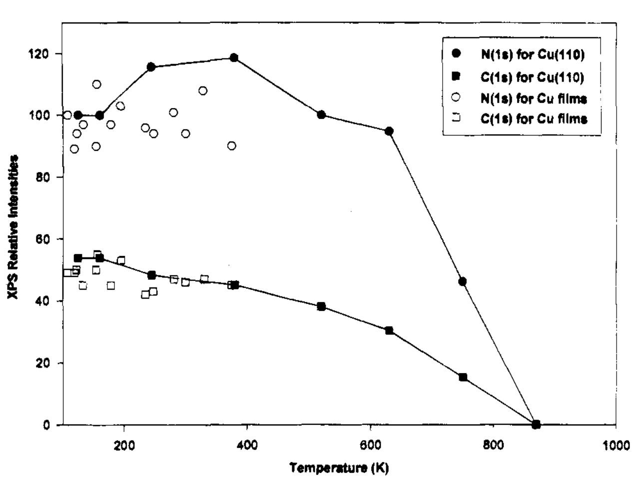

Figure 4. Temperature dependence of the relative surface concentrations of nitrogen and carbon following exposure to diazirine. The solid lines represent data for Cu(110), and the circles and squares represent data for copper films deposited at 107 K. The surface concentration of nitrogen atoms on the Cu(110) at 124 K is 5.7 × 10^{14} atoms cm^{-2}.

Data for the temperature dependent nitrogen and carbon surface concentrations on Cu(110) are shown in Figure 4. Surface concentrations were calculated from the N(1s) or C(1s) peak areas according to the procedure outlined in the Experimental Section. A corresponding set of data for diazirine on atomically rough copper films is also shown in Figure 4. The latter set of data set is normalized with respect to the nitrogen concentration measured at 107 K and is uniformly offset so that the nitrogen plots for Cu(110) and for the copper films coincide. The average nitrogen to carbon concentration ratio at 124 K for Cu(110) is ~1.8, which is reasonably close to the expected ratio of 2:1. The nitrogen to carbon ratio at 107 K is approximately 2:1 for the rough copper films at all exposures studied. In the case of the Cu(110) sample, there is an initial small increase in the nitrogen signal and a decrease in the carbon signal in the temperature region below 250 K. These slight changes possibly arise from modifications in the adsorption geometry or order of the surface species because Figure 4 shows that the anomalous behavior was not observed for diazirine on the rough copper films. The surface concentration data for diazirine on the low-temperature deposited copper films clearly show that the calculated nitrogen and carbon surface concentrations remain roughly constant over the range 100−375 K. This confirms that the C(1s) and N(1s) binding energy shifts which occur on annealing to 380 K result from an interconversion of adsorbed species. That is, the observed shifts do not arise from the desorption of either nitrogen or carbon containing molecules. However, H_2 is removed in a desorption limited peak at 330 K, thereby indicating that the binding energy shifts are partly due to dehydrogenation of surface species. Note that Connolly et al.[30] have shown evidence for the room temperature dehydrogenation of HCN on Cu(110). Thus it is plausible that species such as NCH_x, derived from diazirine, undergo dehydrogenation on Cu(110) below 330 K.

The initial decrease in the surface concentrations of carbon and nitrogen which sets in above 400 K correlates with the weak desorption features shown in the inset of Figure 2. The sharper decrease which is observed above 600 K is due to desorption of nitrogen and cyanogen, as shown in Figure 2.

Both the C(1s) and N(1s) signals are completely removed on annealing to above 800 K. Baddorf and Zehner[26] have shown that nitrogen atom dosed surfaces may be cleaned by heating above 800 K. The latter study also showed that both absorption into the bulk and recombinative desorption of nitrogen occur.

The XPS results obtained on annealing cyanogen on Cu(110) at 630 K are compared in Figure 5 with those obtained on annealing adsorbed diazirine at the same temperature. The comparison reveals very similar N(1s) spectra but quite different C(1s) spectra. The adsorbed species produced on annealing diazirine at 630 K displays a C(1s) peak at 286.0 eV, whereas cyanogen produces an asymmetric peak which has a maximum at 284.8 eV. Outka et al.[27] reported a broad (~2.2 eV FWHM) C(1s) peak at 284.8 eV for C_2N_2 on Cu(110), similar to the feature which we observe. The N(1s) binding energy was not included. The latter study showed that cyanogen dissociates

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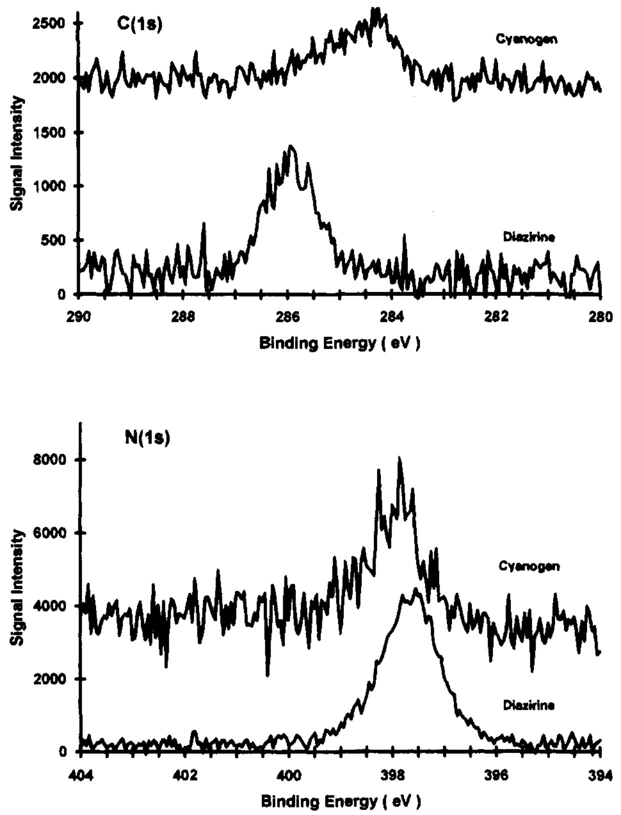

Figure 5. Comparison of XPS data for the adsorption of diazirine and cyanogen on Cu(110). Both sets of data were obtained by exposure to the adsorbate at 124 K, followed by annealing to 630 K.

on Cu(110) and that the recombination of cyano groups yields a cyanogen desorption peak above 800 K. The measured N(1s) binding energy matches the value of 397.6 eV observed by Gudde and Lambert[31] on annealing cyanogen-exposed Ru(100) to 250 K. The results of this XPS calibration study indicate that the surface species giving rise to cyanogen desorption in the diazirine experiments are not identical to the parallel-bonded CN species[30] which are formed by dissociating C_2N_2 on Cu(110).

4. Discussion

The fact that the C(1s) and N(1s) intensities level off for exposures above 0.15 L indicates that there is negligible multilayer adsorption at 124 K. By comparison with previous results[15] for diazirine on Pd(110), the N(1s) spectra taken at 124 K (Figure 3) display features which are not consistent with molecularly adsorbed diazirine. The N(1s) peak at 396.9 eV peak is more than 1 eV lower in binding energy than values observed for molecular diazirine on Pd(110).[15] Furthermore, the TPD data in Figure 2 display only a weak molecular desorption peak, and the XPS data in Figure 4 show no removal of the N(1s) signal below 400 K. Hence, both the XPS and TPD results are consistent with dissociative absorption of diazirine on Cu(110) at 124 K.

The N(1s) spectrum observed at 124 K (Figure 3) is asymmetric and can be synthesized from two peaks placed at 396.8 and 398.1 eV. The asymmetric N(1s) spectrum is attributed to adsorbed atomic nitrogen and species containing CN bonds. Serafin and Friend[32] observed N(1s) peaks at 398.1 and 396.9 eV on annealing HCN-exposed W(100)-(5 × 1)-C at 500 K. The same experiment produced a C(1s) peak at 285.4 eV, in addition to a peak for atomic carbon. Hence, the XPS spectra which we observe for diazirine on Cu(110) at 124 K are remarkably similar to those reported for HCN-derived species on the carbon-modified W(100) surface. Note that Serafin and Friend used HREELS and XPS data to identify the surface species as HCNH and adsorbed atomic nitrogen. By analogy, it is probable that partially hydrogenated species containing CN bonds contribute to the N(1s) intensity at 398.1 eV and to the C(1s) peak at 285.4 eV. Adsorbed atomic nitrogen contributes to the peak at 396.8 eV. N_{ads} on Cu(110) is characterized by a peak in the 396.5−396.8 eV region.[27] The formation of such surface species requires cleavage of the NN bond of diazirine as in reactions 1 or 2.

$$CH_2N_2 \rightarrow N_{ads} + (NCH_x)_{ads} \tag{1}$$

$$CH_2N_2 \rightarrow (NCH_xN)_{ads} \tag{2}$$

From this, we conclude that the observed C(1s) and N(1s) binding energies are consistent with dissociative adsorption of diazirine involving scission of the NN bond. This conclusion is borne out by the TPD data and by other aspects of the XPS data as discussed below. Note that although reaction 1 requires scission of one NN bond and one CN bond, we assume that NN bond scission is the primary decomposition step.

In the context of the question of the bond scission selectivity of copper toward diazirine, the principal TPD peaks show no evidence for the retention of the NN bond. On the contrary, the desorption of cyanogen shows that retention of CN bonds occurs, and the high temperature required for recombinative desorption of N_2 confirms that low-temperature scission of the NN bond takes place. Even the weak desorption features in the 400−500 K region do not show any evidence for NN bond retention. The latter features do not include a $m/q = 28$ peak. On the contrary, they include a $m/q = 26$ peak indicative of CN bond retention.

One may also view the TPD results from the perspective of what would happen if selective CN bond scission actually did not occur. Selective CN bond scission would be expected to produce absorbed methylene species as in reaction 3.

$$CH_2N_{2ads} \rightarrow CH_{2ads} + N_2 \tag{3}$$

However, by comparison to the results of Chiang et al.,[33] the TPD results show no evidence this reaction. The latter authors found that adsorbed methylene, produced by dissociating CH_2I_2, dimerizes on Cu(110) to yield a C_2H_4 desorption peak at 295 K. This result is consistent with the known reactivity of methylene groups on copper.[34] Our TPD spectra do not display any evidence for the desorption of ethylene, and this provides a strong indication that reaction 3 does not take place.

With respect to the dissociative adsorption of diazirine, the XPS provides two additional clear indicators that Cu(110) selectively attacks the NN bond. First, as previously observed[15] for Pd(110), selective CN bond scission would be expected to lead to adsorbed CH_2 and gas phase molecular nitrogen (reaction 3). Adsorbed methylene, or one of its dehydrogenation products, would be characterized by a C(1s) binding energy below 284.0 eV.[15,35] No C(1s) peak close to this region was observed for diazirine on Cu(110), thereby confirming that reaction 3 does not take place. Second, as may be seen from Figure 4, the surface concentration of nitrogen remains ap-

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proximately constant even over the range 124–400 K. This, combined with the fact that the initial low-temperature, [N]/[C] atomic ratio is close to 2, is not consistent with CN bond scission and concomitant low-temperature desorption of N_2, as in reaction 3. In summary, the combined XPS and TPD data conclusively show that selective cleavage of the NN bond (as in reactions 1 or 2) takes place at or below 124 K and that a very large fraction of the resulting molecular fragments eventually desorb above 600 K, as N_2 and C_2N_2.

The selective low-temperature cleavage of the NN bond of diazirine on Cu(110) may be interpreted with reference to previous results for the interaction of diazirine with Pd(110), where both CN and NN bond cleavage were observed to occur in roughly equal amounts.[13,15] As a point of departure, the diazirine–metal interaction will be described in terms of σ-donation and π^*-back-donation in much the same way as CO chemisorption is often described. It is normal to compare these two adsorbates because the HOMO orbital of diazirine lies at approximately 10.75 eV[36] and its empty π^* LUMO orbital is calculated to be a few electron volts above the vacuum level.[37] These values are within 1 eV of the corresponding values for CO.[13] Hence, as in the case of CO, the HOMO and LUMO orbitals have the possibility of undergoing donor–acceptor bond-forming interactions with the metal valence band. However, for a number of reasons discussed below, the σ-donor interaction of diazirine with copper will be weak.

First, the HOMO orbital of diazirine is only weakly resonant with the relatively narrow copper d band.[38,39] As a result, its interaction with the metal may not be strong enough to create an antibonding orbital situated above the Fermi level. If that is the case, HOMO to metal electron transfer is not possible within the framework of the type of four-electron interaction proposed by Andzelm and Salahub[40] and Hoffman.[41] Their model invokes electron transfer from the antibonding component of the HOMO–metal interaction to the lower lying Fermi level. Rangelov et al.[42] have provided experimental validity for such a model in an inverse photoemission study of CO chemisorption on Ni(111) and Pt(111) surfaces.[42] They assigned a feature above the Fermi level, for CO on Pt(111), to an empty 5 σ derived antibonding state. However, a similar state was not observed for CO on Ni(111). This result was interpreted by noting that Ni has the narrower d band and, as a result, the resonant interaction of the HOMO orbital of CO with nickel is weaker than its interaction with platinum. A similar argument may well apply in comparing the interaction of diazirine with copper and palladium. Because the palladium d band is somewhat broader and extends down to lower binding energies than the copper d band,[13] the diazirine HOMO to metal interaction is expected to be stronger on palladium. Thus, according to the four–electron interaction model, charge transfer from diazirine is expected to be weaker on copper than on palladium.

Second, a strong σ-donor interaction is also hindered by the fact that the copper d band is full. The presence of empty d states in the metal valence band may be crucial in permitting a strong donor interaction since it may serve to reduce Pauli repulsion between the closed shell HOMO and the sp free electron gas. Positive overlap between the HOMO orbital of diazirine and appropriate directional d orbitals must contend with Pauli repulsion during chemisorption bond formation. Palladium is more flexible than copper in that it can reduce the repulsive component by a process whereby sp electron density is transferred to empty d levels.[43] Such an electronic configuration change has been invoked as the reason why hydrogen chemisorption is not an activated process on most nickel crystal faces whereas it is on copper surfaces.[44] It has also been emphasized in the context of the chemisorption bond[45] and the interaction of molecules with metal atoms.[46]

With reference to the organometallic literature, a third factor should also be considered. The fact that copper is a weak σ-acceptor is exacerbated by the fact that diazirines are poor σ-donors. The weak donor nature of diazirine is due to the fact that the HOMO orbital is best described as a bonding CN orbital rather than a nitrogen lone pair orbital. The lone pair character of the HOMO orbital of diazirine is calculated to be only 32%.[11] Albini and Kisch[11] predicted that the combination of diazirine, a poor σ-donor molecule, with a poor σ-acceptor metal (such as copper) would favor π-coordination. As shown below, this prediction holds true in case of chemisorption of diazirine on copper.

The analysis given in this paper partly relies on the comparison of the chemisorption of CO with the chemisorption of diazirine. However, we should mention that there exist widely conflicting estimates of the relative importance of σ-donation and π^*-back-donation interactions in the chemisorption of CO on copper. Some theoretical work suggests an important backdonation, from copper to the 2p* orbital of CO, contribution to the interaction.[47] Other experimental and theoretical work suggest a dominant role for 5 σ-donation from CO to copper.[48,49] However, in the context of this paper, we can make the following two assumptions. First, palladium is a better σ-acceptor metal than copper. Second, the combination of poor σ-donor molecule and poor σ-acceptor metal minimizes the extent of a σ-donation interaction between diazirine and copper.

We now turn to the LUMO–metal interaction. The strength of the metal to LUMO interaction will roughly depend on the separation in energy between the π^* affinity level and the copper Fermi level.[50] The position of the π^* electron affinity of diazirine is calculated to be approximately 2.5 eV above the vacuum level.[37] This calculated value is 0.7 eV above the measured π^* affinity level for CO.[51] However, the interaction of metals with the CO π^* orbital is very well documented, and it is generally accepted that this orbital lies close to, or even overlaps, the Fermi level in the case of the chemisorbed molecule.[52] By analogy, the π^* affinity level of chemisorbed diazirine may lie close to the Fermi level. Preliminary results of a density function theory study of the interaction of diazirine with Cu_4 clusters show that a π^*-derived state lies just below the Fermi level.[53] In fact, the observed NN bond scission chemistry also suggests that the LUMO orbital lies at least close

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to the Fermi level. The π^* orbital is antibonding in NN and, hence, it is likely that effective metal to π^* electron transfer is required to produce the NN bond scission which is observed on both Pd(110) and Cu(110). Effective electron transfer to the π^* orbital would rupture the relatively weak NN bond. Note that the NN bond in gas phase diazirine is characterized by a stretching frequency of 1626 cm^{-1},[24] indicating its double bond character.

In comparison to the behavior of diazirine on Pd(110), the interaction of cyclic CH_2N_2 with Cu(110) displays distinct differences in activity and selectivity. Dissociative adsorption occurs at a lower temperature and is totally selective on copper. The observation that diazirine is more reactive on Cu(110) is somewhat surprising since it is a d^{10} metal. However, on the basis of the cluster calculations,[53] the dissociative adsorption of diazirine on Cu(110) may be accounted for by placing the LUMO orbital just below the Fermi level. This would account for the observation that the adsorption of diazirine on copper is dissociative even at the lowest temperatures studied, which is 107 K in the case of copper films. Then, the difference in reactivity between Cu(110) and Pd(110) may possibly be a consequence of the fact that the work function of Pd(110) is 0.7 eV greater than that of Cu(110).[54] This difference could place the LUMO orbital above the Fermi level in the case of Pd(110). Nevertheless, it is unlikely that the difference in work function accounts for the different chemistry observed on the two metals. For reasons of orbital symmetry, the π^* LUMO orbital is expected to interact with the d_π rather than the p_π orbitals of the metal. However, the d band of copper actually lies below the Fermi level of palladium. As a result, it is probably not correct to base an explanation solely on the different work functions. A similar argument was advanced by Sexton and Hughes in a comparison of the chemisorption of unsaturated molecules on copper and platinum surfaces.[17]

In order to explain the observed bond scission selectivity on copper, we have to take into account the fact that the cyclic nature of the HOMO orbital implies an interdependence between the CN and NN bonds. Since the HOMO orbital is bonding in CN and antibonding in NN, a HOMO to metal donor interaction is expected to lower the CN bond order and to raise the NN bond order.[1,13,15] For example, density functional calculations[53] show that the NN bond is contracted by 5% and the CN bonds extended 6% in the first ionization state of diazirine. The stronger donor interaction, relative to copper, which is possible on palladium, then makes the NN bond more difficult to break and the CN bonds easier to break on Pd(110). Hence, as observed experimentally, both decomposition processes becomes possible on palladium, the metal on which the HOMO to metal donor interaction is greatest.

The latter comparison between the two metals can also be phrased in terms of an antisynergistic π-σ bonding interaction.[13] The σ-donor interaction should increase the NN bond order by decreasing the population of the HOMO level. This in turn will cause a destabilization of the π^* orbital, reflecting the shortened NN bond, and thereby push it up with respect to the Fermi level. Thus strong σ-donation leads to weaker back-donation as the separation between the Fermi level and the π^* affinity level increases. On Cu(110), the donor interaction is weak and, hence, the π^* level is located close enough to the Fermi level to favor metal to transfer. The weaker σ-donor interaction with copper thereby causes a stronger acceptor interaction. This description of the chemisorption of diazirine contrasts with the synergistic $\pi-\sigma$ interaction which is often used to describe CO adsorption on metals.[55] The synergistic $\pi-\sigma$ bonding metal, which is borrowed from the organometallic literature, proposes that σ-donation reinforces π-back-donation and vice versa. For example, in the case of metal carbonyls, π-back-donation renders the CO ligands more negatively charged and hence enhances their donation ability.[56] The antisynergistic bonding which we propose for adsorbed diazirine reflects the complexity of the CH_2N_2 molecule and, in particular, the cyclic character of the HOMO orbital.

As pointed out in the Introduction, a principal reason for doing chemisorption studies of diazirine on metals is to selectively generate surface methylene species. This requires selective scission of the CN bonds. On the basis of the antisynergistic model proposed above, platinum or ruthenium would seem like good candidates for selective CN bond cleavage. For example, Pt possesses a relatively wide d band;[39] hence, a strong resonant interaction with the HOMO orbital of diazirine would be expected. This would lead to enhanced molecule-to-metal charge transfer. Furthermore, the relatively greater spatial extension of the d orbitals would maximize repulsion with respect to the filled π orbitals of diazirine and hence favor a tilted adsorption geometry. As discussed above, these factors will facilitate a σ-donor interaction with the metal and weaken the π^*-back-donation component. Finally, Pt(111) possesses a work function of 6.2 eV and this will further serve to minimize back-donation into the π^* LUMO orbital. Similar arguments apply in the case of the chemisorption of diazirine on ruthenium surfaces.

5. Conclusions

This study of the interaction of diazirine with Cu(110) shows that dissociative adsorption via totally selective cleavage of the NN bond occurs at 124 K. The resulting surface species lead to the desorption of H_2 at 335 K and N_2 and C_2N_2 above 700 K. The selective NN bond cleavage is consistent with a predominant metal to π^* chemisorption bond component. By extension, the less selective bond scission previously reported for Pd(110) is consistent with both diazirine to Pd σ-donation and metal to π^*-back-donation. The comparison of the results for Pd(110) and Cu(110) leads to the proposal that the diazirine metal interaction may be usefully described in terms of antisynergistic $\pi-\sigma$ bonding. In general, the study shows that diazirine is a sensitive, albeit complex, probe of the charge redistributions which occur on chemisorption.

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