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Surface Chemistry of Alkyl Amines. 1. Ethylamine and Triethylamine on W(100), W(100)-(5 × 1)-C, and W(100)-(2 × 1)-O

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Abstract: The chemistry associated with ethyl- and triethylamine adsorbed on W(100), W(100)-(5 × 1)-C, and W(100)-2 × 1)-O surfaces has been investigated with use of temperature-programmed reaction spectroscopy and isotopic labeling methods. The reactivity and selectivity for C-C and C-N vs. C-H bond activation is altered on W(100) by the presence of the carbide and oxide overlayers and the extent of amine substitution. Irreversible decomposition predominates on W(100) at low exposures for both amines. Large ethylamine exposures yield trace quantities of CH_4 and NH_3 but no C_2-hydrocarbons on W(100). Triethylamine undergoes C-N and C-C bond cleavage reactions to produce small amounts of ethylene and methane, respectively, on W(100) at high exposure. In contrast, no C-C bond scission products are observed from $(C_2H_5)_3N$ on W(100)-(5 × 1)-C: ethylene and acetonitrile are produced. As on clean W(100), ethylamine does not yield C_2-hydrocarbons resulting from C-N bond scission on the -(5 × 1)-C: acetonitrile is the major product from ethylamine reaction on this surface. The W(100)- (2 × 1)-O surface is inert with respect to C-H, C-N, or N-H bond scission, resulting primarily in molecular ethylamine desorption up to 550 K corresponding to a desorption energy of 33 kcal/mol. The pattern of reactivity is that facile irreversible amine decomposition predominates on initially clean W(100). At high exposures, the W(100) surface is passivated, these inducing chemistry more similar to the -(5 × 1)-C surface. The -(5 × 1)-C strongly bonds the amine exhibiting reactivity consistent with initial selective α-C-H bond activation. The most electron deficient -(2 × 1)-O surface strongly bonds ethylamine but is ineffective in inducing any of the competing types of bond activation.

The investigation of the reactions of organic amines on transition-metal surfaces is of interest technologically and scientifically for gaining an understanding of basic principles governing reactivity and selectivity in surface chemistry at the molecular level. Organic amines are used in heterogeneous catalysis to improve the selectivity in hydrogenation reactions.[1] In addition nitrogen bases are used to titrate the surface area of active sites for a specific catalytic reaction[2] and as corrosion inhibitors.[3] Thus, characterization of the surface chemistry of organic amines is important in understanding the mechanism of their role in technologically important processes.

From the point of view of surface chemistry, organic amines may yield insight into what factors control reactivity and selectivity in bond activation in organic bases. Four competing types of bond activation are possible in alkyl amines: C-N, C-C, C-H, and N-H, which lead to different surface intermediates with varied bonding to the surface, resulting in different products. Reactivity and selectivity are dictated by the relative energetics and extent of reversibility for the various competing bond activation processes. Thus, characterization of these competing processes is important.

This study is one of two undertaken to compare the surface chemistry associated with simple alkyl amines on W(100) to that on W(100)-(5 × 1)-C and W(100)-(2 × 1)-O. In this paper, the chemistry associated with ethylamine, $C_2H_5NH_2$, and triethylamine, $(C_2H_5)_3N$, on these surfaces is characterized. The monoethyl- and triethylamines are compared in order to elucidate the role of N-H bond activation in controlling the observed chemistry.

Nitrogen-hydrogen bond activation in ammonia is known to be facile on W(100)[4] and W(100),[5] occurring to a large extent below 300 K. However, there is precedent for carbon and oxygen overlayers on tungsten stabilizing molecular NH_3 on the surface.[5,6] The initial bonding of both molecular ammonia and alkyl amines to transition-metal surfaces is expected to be primarily via a Lewis base interaction through the nitrogen lone pair. This expectation has been substantiated with both chemical[7-9] and spectroscopic[5,10-12] methods on a range of different surfaces. In analogy to NH_3, N-H bond scission may be anticipated in mono- or disubstituted amines, as proposed for methylamine[7] and ethylamine[8] on evaporated metal films.

On the basis of these previously reported results the presence/absence of amino hydrogens in alkyl amines is expected to affect their stability with respect to surface decomposition and the selectivity for C-N vs. C-C bond activation. Similarly, the presence of the carbide overlayer is anticipated to limit the extent of irreversible N-H bond activation, in analogy to the observed behavior of NH_3.[5,6]

Experimental Section

All experiments were performed in a stainless steel ultra-high vacuum system with a working base pressure of 2×10^{-10} Torr, described previously.[13]

The W(100) surface was cleaned by a sequence of oxygen treatments at a pressure of $\approx 1 \times 10^{-7}$ Torr and a crystal temperature of ≈ 1400 K and subsequent flashing to 2500 K in vacuo. The -(5 × 1)-C overlayer was prepared by exposing clean W(100) maintained at 1500 K to a 60-L dose of ethylene. The -(2 × 1)-O overlayer is prepared by exposure of clean W(100) to 20 L of O_2 at a crystal temperature of 1250 K. Surface cleanliness and order were monitored with retarding field Auger electron spectroscopy and low energy electron diffraction (LEED), respectively.

A directed doser, consisting of a leak valve and a stainless steel doser ($^3/_8$ in. o.d. × $^7/_{16}$ in. i.d.) welded to a 2.75-in. diameter double-sided conflat flange and positioned approximately $^1/_{16}$ in. from the crystal face during dosing, was used to introduce the amines. This configuration allowed for use of relatively high amine pressures in the sample introduction manifold and, thus, minimized the fraction of contaminants, such as H_2O, that were found to be displaced from the doser walls. All other gases were introduced through separate calibrated beam dosers, described in detail elsewhere.[14]

Amines that were not isotopically labeled were obtained commercially and were used without further purification: ethylamine (99.0% purity)

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Table I. Fragmentation Patterns for Alkyl Amines

	rel ion intensities: mass/charge ratio									
molecule	101	86	73	59	58	45	44	31	30	28
$C_2H_5NH_2$[a]						19	20		100	37
$(C_2H_5)_2NH$[b]			21		100		29		98	37
$(C_2H_5)_3N$[a]	5	49		3	65		33		100	51
$(CH_3)NH_2$[a]								57	100	88
$(CH_3)_2NH$[b]						56	100		4	26
$(CH_3)_3N$[a]				44	100				63	30

[a] Data obtained with experimental configuration described herein. [b] Literature data.[32]

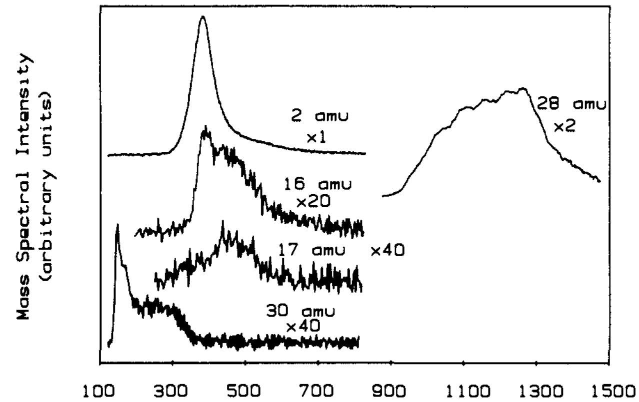

Figure 1. Thermal reaction of ethylamine on W(100). The data shown are for a 5.0-L dose at 120 K crystal temperature. Ethylamine (30 amu), ammonia (17 amu), methane (16 amu), molecular hydrogen (2 amu), and nitrogen (28 amu) are desorbed. Mass 30 is attributable solely to ethylamine desorption, based on desorption data not depicted, of other characteristic ions (Table I). The heating rate below 700 K is 15 K/s. Electron bombardment heating is used to desorb N_2 at high temperature at a rate of 20–40 K/s. Note that the 30 amu ion intensity for coverages on the order of monolayer is small compared to H_2. the presence of multilayer peaks may be used as a gauge of monolayer intensity in the chemisorbed peaks.

from Aldrich and triethylamine (99.0% purity) from Fischer. Isotopically labeled amines were prepared by reaction of the corresponding hydrochloride with an excess of NaOH in water and were subsequently dried with CaH_2 and vacuum distilled. Both the $H_3C^{13}CH_2NH_2{\cdot}HCl$ (99% purity) and $C_2H_5{}^{15}NH_2$ HCl (99% purity) were obtained from ICON Isotopes.

Thermal reaction data were obtained with a quadrupole mass spectrometer (UTI 100C) controlled by an IBM PC, described previously.[14] The mass spectrometer was enclosed in a cryogenic shield. A flag with an orifice of 0.0625-in. diameter and positioned less than 0.125 in. from the crystal face was rotated in front of the mass spectrometer ionizer during thermal reaction experiments in order that only line of sight desorption products be detected.[15] This precludes background reaction or desorption from contributing to the observed spectra. Mass spectral data for ethylamine and triethylamine are presented in Table I. Several amine fragment ions were monitored in given experiment in order to unambiguously determine the identity of the desorbing species. Thermal desorption data are presented for the most intense ion in the spectrum although other characteristic ions were, in general, monitored.

Results

Ethylamine on W(100). The temperature programmed reaction spectrum following exposure of W(100) to 5.0 L of ethylamine is represented in Figure 1 with ethylamine, methane, ammonia, molecular nitrogen, and hydrogen observed as volatile products. No other products were detected;[16] most notable was the absence of C_2-hydrocarbons.

Table II. Methane Products from Reaction of Adsorbed Atomic Deuterium and Ethylamine

mass	major[b] ion	rel intensity
16	CH_4^+	1.0
17	CH_3D^+	0.4
18	$CH_2D_2^+$	0.15
19	CHD_3^+	0.15
20	CD_4^+	0

[a] The ratio of surface D:H is 0.37. [b] The relative intensities are uncorrected for fragmentation in the mass spectrometer.

Ethylamine ($C_2H_5NH_2$) exposures of less than 2.0 L result exclusively in irreversible decomposition on the W(100) surface, yielding gaseous H_2 and N_2 at 400 and >1000 K, respectively. The observation of only desorption limited H_2 peak is consistent with complete dehydrogenation below 400 K, setting an upper bound on the E_a for irreversible dehydrogenation of 24 kcal/mol. At exposures above 2.0 L, trace amounts of CH_4 are produced at 400 K with a shoulder developing at 450 K above 2.5 L. A small amount of NH_3 formation is detected at 450 K for exposures above 2.5 L.[17] Reaction of $C_2H_5{}^{15}NH_2$ verifies that both methane and ammonia are formed. The production of methane and ammonia increases up to an exposure of 5.0 L. Desorption of the parent, ethylamine, commences at exposures ≥2.5 L; initially, at 325 K ($E_d \approx 19$ kcal/mol),[33] then at 170 K (exposure ≥ 4.0 L), and subsequently at 150 K. The 150 K desorption peak does not saturate, allowing assignment of the peak as sublimation of a condensed multilayer. Carbon remains on the surface subsequent to thermal reaction up to 1500 K, determined with Auger electron spectroscopy. Nitrogen is quantitatively removed via thermally induced atom recombination above 1000 K.

Thermal reaction of coadsorbed atomic deuterium and $C_2H_5NH_2$ was effected in order to infer the origin of the methane produced and to probe for reversible hydrogen atom abstraction in the desorbed ethylamine. The mass spectral data obtained from the D + $C_2H_5NH_2$ reaction are summarized in Table II. The primary isotopes of methane produced are CH_3D and CH_4 in a ratio of 0.37. Likewise, the ratio of D:H that desorbs as H_2, D_2, or HD is 0.37, suggesting that methane formation proceeds via hydrogenation of the methyl group in ethylamine with surface hydrogen (deuterium). No shifts in the temperature of the different methane or ammonia isotopes formed in the deuterium–ethylamine coadsorption experiment were observed. Reaction of $H_3C{-}^{13}CH_2{-}NH_2$ did not produce any detectable $^{13}CH_4$ confirming the assertion that methane is formed from hydrogenation of the methyl group. In the coadsorption of deuterium and ethylamine, CH_2D_2 and CD_3H were also produced and are attributed to reversible H–D exchange in the methyl group prior to hydrogenation. The absence of CD_4 production in the D + $C_2H_5NH_2$ reaction and lack of $^{13}CH_4$ formation from $H_3C{-}^{13}CH_2NH_2$ render rehydrogenation of adsorbed carbon an unlikely reaction pathway. It is important to note that preadsorption of large amounts of atomic deuterium or hydrogen reduced the relative amount of methane formed with respect to ethylamine desorption. This may be the result of hydrogen induced recon-

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[15] Pump out holes (≈1.0 cross-sectional diameter) were positioned at the base of the cryoshield to preclude a pressure buildup in the region of the mass spectrometer during the course of an experiment.

[16] A search for reaction products was performed both by monitoring discrete masses and by using a broad range spectral search where masses 12–90 were monitored in a single experiment.[24] The ions monitored in the discrete experiments are listed below: 45, 30, 28, and 15 amu; 16, 17, and 18 amu; 26, 27, and 31 amu; 40, 41, and 42 amu; 44, 45, and 58 amu; and 59, 73, and 86 amu.

[17] This NH_3 desorption is at a higher desorption following exposure of ammonia to W(100) both in this work and in previously reported work.[4] Thus, this product is not attributable to contamination of the amine with ammonia but is formed in a surface reaction.

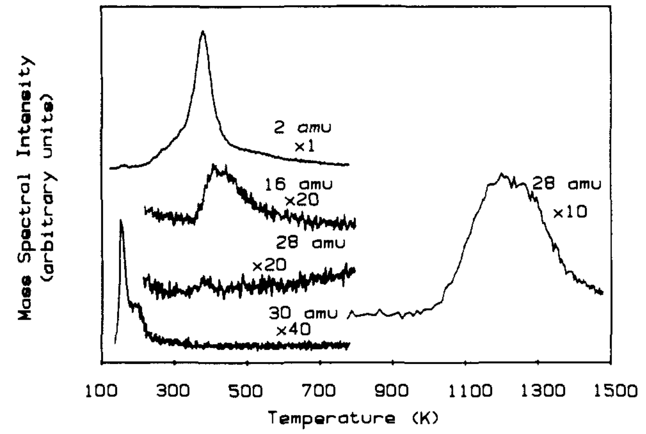

Figure 2. Triethylamine reaction on W(100). Triethylamine (30 amu), ethylene (28 amu), methane (16 amu), and H_2 (2 amu) production is observed below 700 K with radioactive heating (d*t*/d*t* = 15 K/s). Electron bombardment heating induces molecular nitrogen (28 amu) desorption at high temperature. The initial triethylamine dose in this experiment was 5.0 L at 120 K crystal temperature.

struction of the W(100) surface,[18] or site blocking, either of which may affect the extent of C–C bond cleavage. This effect was not investigated in detail. No deuterium incorporation into desorbing ethylamine was detected in the coadsorption experiments. The NH_3 isotopic distribuion was not quantitated due to the low signal levels.

Triethylamine on W(100). The reaction of triethylamine was investigated in order to identify the role of N–H bond activation in determining the product distribution for ethylamine reactions on tungsten. Temperature-programmed reaction data obtained from $(C_2H_5)_3N$ are shown in Figure 2. As in the case of monoethylamine, triethylamine undergoes irreversible decomposition on W(100), yielding desorption limited gaseous H_2 and N_2 at 400 and 1200 K, respectively, and residual surface carbon, setting an upper limit for the activation energy for irreversible C–H bond cleavage of 24 kcal/mol. Higher exposures (>1.5 L) result in desorption of molecular $(C_2H_5)_3N$ at 200 K and subsequently at 160 K for exposures ≥2.5 L. The 160 K peak does not saturate and is attributed to sublimation of condensed triethylamine. The approximate desorption energy of the 200 K state is 12 kcal/mol.

Methane is produced in approximately the same absolute amount from the triethyl- vs. monoethylamine at higher coverages (Figure 2). Methane formation is observed for triethylamine exposures greater than 2.2 L at 390 K and reaches a maximum at $(C_2H_5)_3N$ exposures of 7.5 L. The energetics for CH_4 formation are essentially the same for reaction of triethyl- and ethylamine, based on the CH_4 peak temperature.

There are two qualitative differences in the chemistry of tri- vs. monoethylamine on W(100): A trace quantitaty of ethylene is produced from C–N bond scission in triethylamine while NH_3 was not. Ethylene formation was observed in a reaction limited peak at 390 K,[19] just prior to CH_4 formation. The absence of NH_3 formation from $(C_2H_5)_3N$ is not surprising in that three C–N bonds must be cleaved and three N–H bonds formed. The total amount of H_2 production from triethylamine decomposition is approximately the same as for ethylamine (Figures 1 and 2). Consistent with this observation, the quantity of N_2 produced from decomposition of $(C_2H_5)_3N$ is approximately one-third that for ethylamine. These observations are consistent with a fixed total amount of atomic carbon and nitrogen produced from reaction of both ethyl- and triethylamine on initially clean W(100). The expected ratios for triethyl- vs. ethylamine for a 1:1 ratio of (C + N) atom production are 5:3 and 1:3 for H_2 and N_2 production, respectively, in reasonable agreement with the experimentally determined values. This is similar to carbon and oxygen blocking the dissociation of CO on W(100) which has been previously documented.[20]

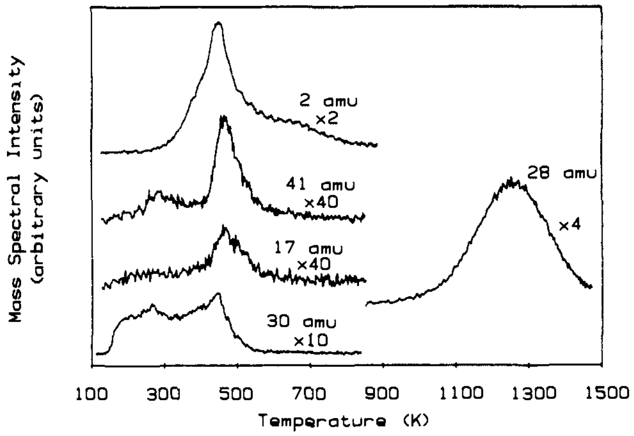

Figure 3. Thermal desorption data obtained subsequent to a 3.3-L dose of $C_2H_5NH_2$ on W(100)-(5 × 1)-C. Ethylamine (30 amu), NH_3 (17 amu), acetonirile (41 amu), and H_2 (2 amu) are detected below 900 K where d*T*/d*t* = 15 K/s. Molecular nitrogen (28 amu) desorption occurs above 1000 K.

Ethylamine on W(100)-(5 × 1)-C. Temperature-programmed reaction data obtained from reaction subsequent to a 3.3-L exposure of $C_2H_5NH_2$ to W(100)-(5 × 1)-C is shown in Figure 3. The observed desorption products are ethylamine, acetonitrile, ammonia, molecular hydrogen, and nitrogen. No other products were detected; most notably CH_4 and HCN were not observed.

At low exposures (≤0.25 L), irreversible decomposition of ethylamine occurs, producing exclusively H_2 and N_2 at 450 and ≥1300 K, respectively. The total amount of irreversible decomposition at at reaction saturation is approximately one-half as large on the -(5 × 1)-C compared to initially clean W(100), as measured from the H_2 and N_2 integrated intensities (Figures 1 and 3). Heating of the overlayer produced by $C_2H_5NH_2$ on the -(5 × 1)-C surface to 1500 K in a thermal desorption experiment regenerated the -(5 × 1)-C low energy electron diffraction pattern with no residual nitrogen detectable with Auger electron spectroscopy. The chemistry associated with the -(5 × 1)-C surface is the same subsequent to thermal reaction, indicating that there is no significant alteration of the surface.

Above 0.25 L exposure, desorption of ethylamine commences with a peak centered at 475 K corresponding to an approximate desorption energy of 28 kcal/mol.[33] Higher exposures result in a broad ethylamine desorption in the range of 180–500 K, consisting of at least three unresolved features.[21] Exposures above 4.0 L result in sublimation of $C_2H_5NH_2$ multilayers at 150 K.

The onset of acetonitrile and ammonia desorption occur at an ethylamine exposure of 0.5 L. Both desorptions are centered at 490 K. The coincidence of the $C_2H_5NH_2$, CH_3CN, and NH_3 is consistent with their being formed from a common surface intermediate. Acetonitrile production from $C_2H_5NH_2$ is observed in the same temperature regime in which acetonitrile normally desorbs from W(100)-(5 × 1)-C.[22] When acetonitrile is dosed on the -(5 × 1)-C surface it exhibits reversible exchange of the methyl hydrogens in the acetonitrile at 400 K which desorbs up to 550 K. Thermal treatment of adsorbed ammonia on the carbide surface yields poorly resolved NH_3 desorption peaks in the temperature range of 200–450 K.

Triethylamine on W(100)-(5 × 1)-C. Temperature-programmed reaction data obtained subsequent to exposure of W(100)-

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(21) The breadth of the amine desorption features is not a result of background desorption desorption or instrumental limitations.[15] Lower amine exposures yield desorption features ≈25 K in width. The broad desorption features appear at higher exposures and most likely result from a multitude of desorption energies possibly due to intermolecular interactions.

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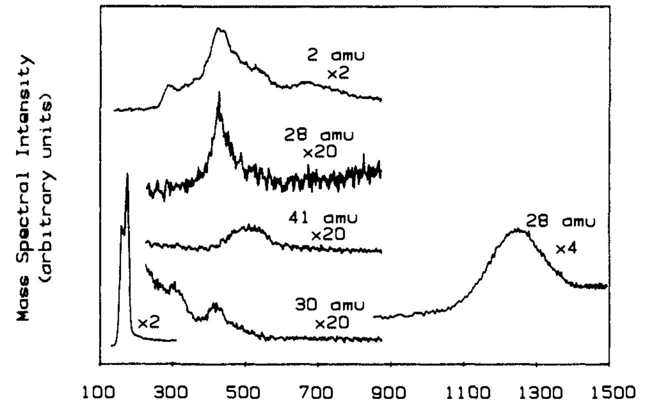

Figure 4. Triethylamine thermal reaction data on W(100)-(5 × 1)-C. Thermal treatment of a 6.6-L dose of $(C_2H_5)_3N$ adsorbed at 120 K results in desorption of $(C_2H_5)_3N$, ethylene (28 amu), acetonitrile (41 amu), and molecular hydrogen (2 amu) below 800 K. N_2 (28 amu) formation is evident above 1000 K where electron bombardment heating is used.

(5 × 1)-C to 6.6 L of triethylamine are shown in Figure 4. Triethylamine, ethylene, methane, acetonitrile, molecular hydrogen, and nitrogen are produced, as described below. No other products are observed,[16] in particular NH_3 is not produced.

As in the case of monoethylamine, $(C_2H_5)_3N$ undergoes initial irreversible decomposition resulting in production of $N_2(g)$ and $H_2(g)$. (Figure 4). The total amount of irreversible decomposition is approximately the same as for triethylamine reaction on initially clean W(100) based on integrated N_2 intensities. Sequentially higher exposures result in desorption of molecular triethylamine[20] at 325, 425, 170, and 160 K commencing at exposures of 1.0, 1.5, 2.0, and 3.0 L, respectively. The 160 K desorption peak is attributed to condensed multilayers. The highest temperature molecular desorption peak corresponds to an activation energy for desorption of approximately 25 kcal/mol.

Production of ethylene, acetonitrile, and trace amounts of methane commences at $(C_2H_5)_3N$ exposures of 1.5 L, as shown in Figure 4. Ethylene desorbs in a reaction limited peak[19] at 425 K, coincident with the highest temperature triethylamine desorption and a reaction limited molecular hydrogen peak.[20] CH_3CN desorption is observed at ≈525 K, coincident with an unresolved reaction limited H_2 peak.

No increase in the intensity of any of the reaction products was observed at exposures greater than 2.0 L. The absolute amount of irreversible decomposition to form molecular hydrogen and nitrogen at a saturation exposure of $(C_2H_5)_3N$ is comparable on the -(5 × 1)-C and W(100) surfaces. The significant differences in the chemistry of the W(100)-(5 × 1)-C compared to W(100) are the increased extent of ethylene production with respect to CH_3CN formation, the desorption of triethylamine at higher temperature (425 vs. 200 K), and the accompanying production of H_2 in reaction limited peaks at 425, 525, and 675 K on the -(5 × 1)-C surface. The coincidence of molecular hydrogen peaks with specific products of varying relative hydrogen content suggests that surface stable fragments are undergoing sequential stepwise dehydrogenation reactions. This is in contrast to the reaction of ethylamine on W(100)-(5 × 1)-C where all products are formed at the same temperature, indicating that they originate from a common intermediate.

Ethylamine on W(100)-(2 × 1)-O. The W(100)-(2 × 1)-O surface prepared in this work has been extensively studied with a range of techniques.[25-28] As in the case of the -(5 × 1)-C surface, tungsten atoms undergo a reconstruction with some incorporation of oxygen beneath the topmost metal layer. The proposed structure is represented in Figure 5.

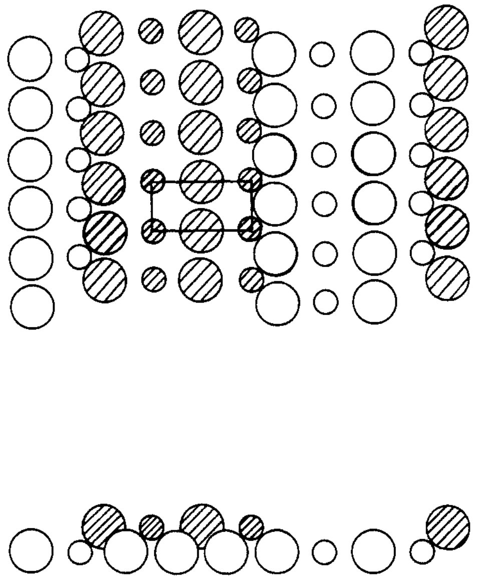

Figure 5. Model of a W(100)-(2 × 1)-O surface. Small circles represent oxygen atoms with shaded circles denoting atoms lying above the plane of the drawing. The lower part of the figure is a side view of the surface region. This model has been previously proposed in the literature.[25,28]

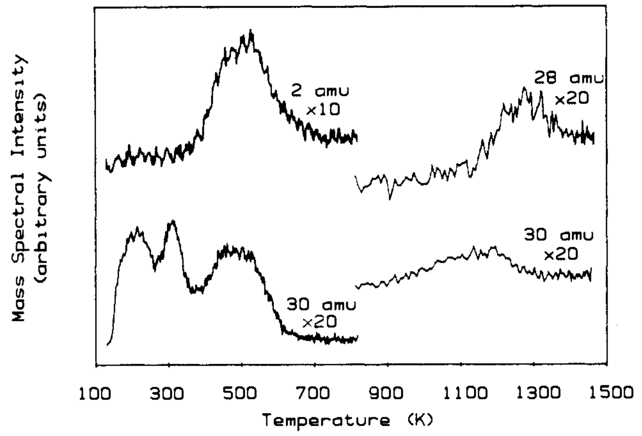

Figure 6. Ethylamine thermal desorption from W(100)-(2 × 1)-O.[18] Mass 30 corresponds to amine desorption below 700 K and 2 amu to molecular hydrogen production. $C^{18}O$ (30 amu) and N_2 (28 amu) desorption are induced above 1000 K with electron bombardment heating. The initial ethylamine dose was 6.0 L in this experiment.

Temperature-programmed reaction data obtained for ethylamine adsorbed on W(100)-(2 × 1)-O are shown in Figure 5. The total extent of irreversible decomposition or surface reaction is approximately 0.10 and 0.20 compared to that on W(100) or W(100)-(5 × 1)-C, respectively. The only desorption products in a thermal reaction experiment that are observed are ethylamine, molecular hydrogen, nitrogen, and CO.[16]

Ethylamine desorption from the -(2 × 1)-O surface is observed even below 0.10 L initial exposure, centered at 550 K corresponding to E_d ≈33 kcal/mol. increasing ethylamine exposure results in molecular desorption at temperatures below 500 K, with essentially continuous desorption observed in the range of 150–550 K above 0.6 L.[20] The maximum temperature at which molecular desorption is observed on the -(2 × 1)-O is 100 and 200 K higher than on W(100)-(5 × 1)-C and W(100), respectively.

Consistent with the relatively high temperature at which molecular desorption is observed, there is only a limited amount of decompostion. The decomposition products are molecular hydrogen, nitrogen, and CO from atom recombination with desorption peaks centered at 500, 1250, and 1200 K, respectively, at saturation. No other reaction products are observed indicating

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Table III. Highest Temperature Molecular Amine Desorption at Saturation and Corresponding Desorption Energies

	amine			
surface	$C_2H_5NH_2$	(E_d, kcal/mol)	$(C_2H_5)_3$	(E_d, kcal/mol)
W(100)	325 K	(19)	200 K	(12)
W(100)-(5×1)-C	475 K	(28)	425 K	(25)
W(100)-(2×1)-O	550 K	(33)		

that the -(2 × 1)-O is relatively ineffective in inducing C-H, N-H, and C-N bond activation in ethylamine. The reaction of triethylamine was not investigated on the -(2 × 1)-O surface.

Discussion

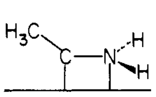
The reactivity and selectivity associated with mono- and triethylamine on W(100) is dependent on both the presence of the carbide overlayer and the presence/absence of amino hydrogen atoms. The most striking aspect of the results reported herein is the increased activation energy for decomposition of ethyl- and triethylamine on the -(2 × 1)-O and -(5 × 1)-C surfaces compared to W(100). Irreversible decomposition predominates at low coverage on initially clean W(100). Buildup of atomic carbon, nitrogen, and hydrogen "passivated" the surface such that its chemistry is similar to the carbide. This is analogous to passivation of W(100) via nitrile decomposition. As summarized in Table III, the maximum temperature at which molecular amine desorption is observed is considerably higher on the -(2 × 1)-O and -(5 × 1)-C than on W(100). In addition, desorption limited molecular hydrogen is observed at 390 K on W(100) from reaction of both $C_2H_5NH_2$ and $(C_2H_5)_3N$. Both pieces of evidence signify that irreversible decomposition occurs below 300 K at low exposures on W(100) for both amines. In contrast, molecular amine adsorption persists, in part, on the carbide and oxide surfaces.

Differences in the chemistry of the trialkyl- and monoalkylamines are also observed. Triethylamine undergoes C-N bond cleavage, yielding C_2H_4, on both W(100) and W(100)-(5 × 1)-C. In contrast, no hydrocarbon products resulting from C-N bond scission in ethylamine are detected on either the W(100) or the carbide surfaces. Monoethylamine yields ammonia in a reaction limited peak on W(100)-(5 × 1)-C whereas no ammonia production is evident from reaction of triethylamine on either W(100) or W(100)-(5 × 1)-C. These results may be accounted for in terms of initial α-C-H activation, discussed below.

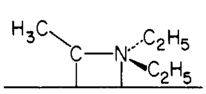
In addition to the differences between the chemistry of $C_2H_5NH_2$ and $(C_2H_5)_3N$, there are significant differences in the product distributions on the carbide and oxide surfaces compared to initially clean W(100). Acetonitrile formation and desorption are observed from the reaction of both mono- and triethylamine on the -(5 × 1)-C surface at 490 and 525 K, respectively, with $C_2H_5NH_2$ yielding a larger amount of CH_3CN than $(C_2H_5)_3N$. However, no acetonitrile desorption is detected for either the mono- or trisubstituted amine reacting on W(100). Instead, C-C bond scission and hydrogenation to form methane occur in both $C_2H_5NH_2$ and $(C_2H_5)_3N$ on W(100) at high coverages. Analogous selectivity changes are observed for C-C bond cleavage vs. desorption of acetonitrile[22] itself on W(100) compared to W(100)-(5 × 1)-C. Methane is produced from hydrogenation of the methyl group in CH_3CN on W(100) while no methane is produced on the carbide. As in the case of ethylamine, methane formation is proposed to proceed primarily via hydrogenation of the methyl group in acetonitrile. The -(2 × 1)-O surface does not yield any hydrocarbon products from surface reaction, consistent with the limited amount of decomposition.

The extent of C-N bond activation leading to hydrocarbon formation in triethylamine is also greater on the -(5 × 1)-C than on W(100). The temperature where ethylene is formed from $(C_2H_5)_3N$ is also different: 425 and 390 K for W(100)-(5 × 1)-C and W(100), respectively. The increased extent of ethylene formation occurring on the -(5 × 1)-C is consistent with the smaller extent of irreversible C-H bond scission on the carbide vs. W(100), precedented in previously reported chemical studies.[13,21]

The differences in product distribution observed for the triethyl- and monoethylamines on W(100) and W(100)-(5 × 1)-C surfaces may be related to the nature of the initial bond cleavage steps that occur. Initial bonding of both alkylamines to the surface is expected to proceed via the nitrogen lone pair, as discussed in the introduction. Subsequently, cleavage of α-C-H bonds is expected to compete with N-H or C-N bond scission in the mono- or triethylamine, respectively. Initial C-H bond breaking at the α-position results in a surface intermediate of the nature **1a** and **1b** for mono- or trisubstitution, respectively.

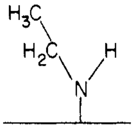


1a

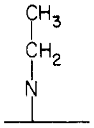


1b

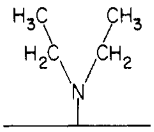
Alternatively, initial N-H bond activation in ethylamine yields intermediates similar to **2a** or **2b**. Analogously, initial C-N bond cleavage in triethylamine would result in intermediate **3**.



2a



2b



3

Initial α-C-H bond activation yielding intermediate **1a** or **1b** may be used to account for all observed products. Carbon-nitrogen bond scission in the triethylamine derived intermediate, **1b**, yields ethylene. C-N bond scission and hydrogenation of the ethylamine derivativate, **1a**, forms NH_3. Lastly, elimination of both amine hydrogens or both ethyl groups from intermediates **1a** or **1b**, respectively, results in formation of acetonitrile. Hydrogenation of intermediates **1a** and **1b** regenerates the parent amine.

Selective, reversible α-C-H bond activation is proposed on the -(5 × 1)-C surface for both ethylamine and triethylamine. The reaction data are consistent with formation of intermediate **1a** from ethylamine prior to 475 K which subsequently undergoes competing reaction, as described above, to yield ethylamine, CH_3CN, H_2, and NH_3. In the case of triethylamine, initial α-C-H bond activation is proposed to compete with molecular desorption, accounting for the 325 K H_2 and $(C_2H_5)_3N$ peaks evident in Figure 4. Subsequent C-N and C-H bond scission compete with rehydrogenation of intermediate **1b** to yield H_2, C_2H_4, and $(C_2H_5)_3N$ at 425 K. This is the same temperature regime where reversible C-H bond activation has been documented for CH_3CN on W(100)-(5 × 1)-C. Further, C-N and C-H bond cleavage of the triethylamine-derived fragment yield acetonitrile and H_2 at 525 K.

Initial N-H or C-N bond activation in ethylamine or triethylamine, respectively, to yield intermediates **2** and **3**, followed by α-C-H bond activation also accounts for the observed reaction products. Although NH bond scission is possible, ammonia formation would require an additional hydrogenation step, rendering this scheme less likely. This reaction scheme is analogous to that previously proposed for ethylamine reaction on evaporated transition-metal films.[7] Initial C-N bond cleavage in the triethylamine is not consistent with earlier studies asserting that C-N bond scission is rate limiting in the surface reactions of amines.[7-9]

Discrete osmium and ruthenium complexes of primary and secondary amines are known to undergo facile N-H bond scission to form stable compounds with NR or NRR′ ligands, respectively.[30] These reactions were observed for *n*-propylamine and dimethylamine. No evidence for facile α-C-H bond scission was reported. These results suggest that initial facile N-H bond cleavage will occur in the surface case. However, multicenter metal-C-H bonds are known to form on an extended surface, preceding C-H bond cleavage.[31] Such interactions render facile α-C-H bond activation plausible on a surface even though not observed in the discrete cluster case. The precedent for high activation barriers for N-H bond scission in NH_3 on carbided and oxided tungsten also supports the mechanism proposing initial α-C-H activation.

The importance of the two proposed reaction pathways may also be dependent on the surface composition. As previously stated, irreversible C-H bond scission is known to be limited while selective C-H cleavage is facile for a number of organic molecules on the -(5 × 1)-C surface.[13,19,21] It is, therefore, reasonable to contend that the relative contribution of the various reaction pathways may differ on the surfaces studied; initial α-C-H bond scission best accounts for all observations. However, contributions from reversible N-H and C-H activation cannot be ruled out on the basis of this work. Vibrational studies are planned in order to address these issues.

Previously reported results obtained for ethanol adsorbed on W(100) and W(100)-(5 × 1)-C exhibit analogous selectivity changes.[2,3] Clean W(100) primarily induces initial, irreversible decomposition of C_2H_5OH, which "passivated" the surface. Reaction on the carbide or passivated surface results in more selective chemistry. Adsorbed ethoxy radical is proposed as the reactive intermediate on the carbide or passivated surfaces. The extent of C-C bond cleavage resulting in CH_4 formation is greater on W(100) than on the carbide. Carbon-oxygen bond cleavage in the alkoxide resulting in C_2H_4 and H_2O is also reported, with the selectivity for C-O vs. C-C bond activation being greater on the -(5 × 1)-C compared to W(100). Acetaldehyde is also produced from ethanol reaction on both W(100) and W(100)-(5 × 1)-C, resulting from O-H and α-C-H bond cleavage, a reaction analogous to the formation of acetonitrile in the amine case. Analogous alteration in the extent of C-C bond cleavage was observed for ethylamine. This comparison coupled with results obtained for methyl- and trimethylamine[29] indicates that the observed alteration in reactivity and selectivity is somewhat general.

Conclusions

The reactivity and selectivity associated with triethyl- and monoethylamine has been compared on W(100) and W(100)-(5 × 1)-C and W(100)-(2 × 1)-O. Acetonitrile is proposed as a reactive intermediate on the clean surface. Initial activation may occur at C-H, NH, or C-N bonds. The data presented herein are best accounted for by an intermediate formed via α-C-H cleavage on the -(5 × 1)-C and "passivated" W(100) surfaces, which undergoes further surface reaction. The -(2 × 1)-O surface is relatively inert toward C-H, N-H, or C-N bond cleavage in the amine, although molecularly bound $C_2H_5NH_2$ is strongly bound to the surface. These results are consistent with a general trend in which irreversible, nonselective chemistry predominates on clean W(100). Amine decomposition passivates the W(100) surface. The passivated and carbide surfaces stabilize molecularly bound amine or alkoxide leading to more selective chemistry. Further spectroscopic and specific labeling studies are planned to characterize the nature and energetics of bond cleavage in an effort to rationalize the observed selectivity changes.

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Registry No. $C_2H_5NH_2$, 75-04-7; $(C_2H_5)_3N$, 121-44-8; W, 7440-33-7; C, 7440-44-0; O_2, 7782-44-7.

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Surface Chemistry of Alkyl Amines. 2. Methylamine and Trimethylamine on W(100), W(100)-(5×1)-C, and W(100)-(2×1)-O

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Abstract: The adsorption and reaction of mono- and trimethylamine have been investigated on W(100), W(100)-(5×1)-C, and W(100)-(2×1)-O, using temperature-programmed reaction spectroscopy. Reactivity and selectivity are dependent on the presence of the oxide or carbide overlayers and the degree of substitution of the amine. The activation energy for irreversible C-H bond cleavage in trimethyl- and methylamine was significantly greater on the -(2×1)-O and -(5×1)-C surfaces compared to W(100). Most notable was the elevated temperature up to where molecular amine desorption is observed on the -(2×1)-O: 650 and 600 K for methyl- and trimethylamine, respectively, corresponding to approximate desorption energies of 39 and 35 kcal/mol. The extent of amine substitution also qualitatively alters the product distribution, with CH_4 produced only from $(CH_3)_3N$ and NH_3 only from $(CH_3)NH_2$ on W(100) and W(100)-(5×1)-C. No C-N bond scission products were observed on W(100)-(2×1)-O, consistent with the predominance of reversible molecular adsorption without significant decomposition. Possible reaction mechanisms are discussed in terms of competing C-H, N-H, and C-N bond activation.

The investigation of the reaction of organic amines is of interest in contributing to the understanding of the principles that dictate surface reactivity and selectivity. The reactions of the simplest primary and tertiary amines, $(CH_3)NH_2$ and $(CH_3)_3N$, are well-suited for comparing selectively changes for competing types of bond activation within a molecule. In the reaction of trimethyl- or methylamine, C-H bond scission will compete with C-N and/or N-H bond cleavage, respectively. Thus, selectivity in bond ac-