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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(30) Stone, F. G. A.; Wilkinson, G. *Comp. Orgmet. Chem.* **1981**, *3*, 1025 and references therein.

(31) Demuth, J. E.; Ibach, H.; Lehwald, S. *Phys. Rev. Lett.* **1978**, *40*, 1044.

(32) *Eight Peak Index of Mass Spectra*, 1st ed.; 1970, compiled by Imperial Chemical Industries.

(33) The estimation of desorption energy is based on the assumption of first-order kinetics and a preexponential of 10^{13} s^{-1}.[34]

(34) King, D. A. *Surf. Sci.* **1975**, *47*, 384.

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-

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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.[26]

tivation may be investigated as a function of surface composition and amine substitution. This study is a companion to the investigation of mono- and triethylamine[2] reaction on W(100) and W(100)-(5×1)-C, where C-C bond activation is also possible. In addition, reactivity and selectivity changes in the amines induced by carbide or oxide overlayers may be compared to the analogous alkoxides.[1] This will be used to determine if the observed alteration in surface chemistry by adlayers of oxygen or carbon are generally exhibited by Lewis bases and what effect the strength of Lewis basicity of the adsorbate has on reactivity, selectivity, and adsorption strength.

Methylamine adsorption and reaction has been previously investigated on polycrystalline transition-metal films of Ni[3,4], Fe,[3,4] Pd,[3] and W[3] and on Mo(100),[6] Ni(100), Ni(111), Cr(100), and Cr(111).[5] Trimethylamine studies have been previously reported for Ni and Fe films[4] and Mo(100) and oxidized Mo(100).[6] In all cases, initial adsorption is proposed to occur via a Lewis base interaction of the nitrogen lone pair and the surface, analogous to that observed for NH_3.[7-9] Catalytic reaction of $(CH_3)NH_2$ with hydrogen on transition-metal film yields NH_3 and CH_4 as hydrogenolysis products with C-N bond scission proposed as the rate limiting step with C-H and N-H bond breaking/making occurring on a comparatively rapid time scale.[3]

The effect of carbon and oxygen adlayers on the chemistry of NH_3 on tungsten[7,8] and $(CH_3)_3N$ on Mo(100)[6] has been previously investigated. Ammonia was found to be stabilized with respect to N-H bond scission by the presence of oxygen[7,8] and carbon.[8] Trimethylamine was also found to be stabilized with respect to irreversible decomposition on Mo(100) by preadsorbed oxygen or carbon and nitrogen resulting from initial decomposition of the amine.[6] The rate limiting step is proposed to be C-N bond cleavage in the $(CH_3)_3N$-Mo(100) system.

These previously reported results support the expectation that the reactivity and selectivity associated with methyl- and trimethylamine on W(100) will be altered by oxide and carbide overlayers. Anticipated alteration in the energetics and extent of N-H and C-N bond activation is compared by investigating both the mono- and trisubstituted amine. The results described herein support the contentions that reactivity and selectivity in amines are altered by carbon or oxygen layers and by the extent of amine substitution. Significant differences in the product distributions and reaction energetics are delineated on the three surface and for $(CH_3)_3N$ compared to $(CH_3)NH_2$ in this work.

Experimental Section

All experiments were performed in an ultrahigh vacuum system with a working base pressure of 2×10^{-10} Torr.[2] The procedures used for crystal preparation, cleaning, dosing, and thermal desorption are identical with those described in the companion ethylamine paper.[2] Relevant mass spectral data for several simple alkyl amines are summarized in Table I.

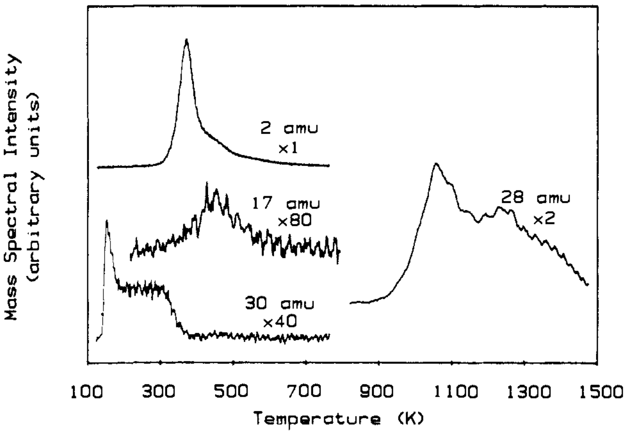

Figure 1. Thermal desorption data obtained subsequent to a 3.0-L dose of $(CH_3)NH_2$ on W(100) at 120 K. Desorptions of $(CH_3)NH_2$ (30 amu), NH_3 (17 amu), H_2 (2 amu), and N_2 (28 amu) are observed. Mass 30 is the most abundant ion in the $(CH_3)NH_2$ mass spectrum. Other relevant ions, not shown, are also monitored in a desorption experiment. Refer to Table I for relative cracking fractions.

Methylamine (98.0% purity), trimethylamine (99.0% purity), and deuterium (99.5% purity) were obtained from Matheson and used without further purification.

Results

Methylamine on W(100). Temperature-programmed reaction data obtained subsequent to a 3.3-L exposure of methylamine to W(100) are presented in Figure 1. The observed products are methylamine, ammonia, molecular hydrogen, and nitrogen. No other volatile products were detected;[10] most notable is the absence of CH_4, HCN, and larger molecular weight amines.

Irreversible decomposition of $(CH_3)NH_2$ predominates on W(100) for exposures less than 0.75 L, yielding $H_2(g)$, $N_2(g)$, and residual surface carbon. Molecular hydrogen production is observed in the temperature range of 325-550 K. The hydrogen desorption features are coverage dependent with peaks centered at 350 and 450 K. Below 0.75 L of $(CH_3)NH_2$ exposure, the area of the two peaks differs roughly by a factor of 2 with the 350 K peak dominating at higher exposures. The molecular hydrogen desorptions are attributed to recombination of surface atomic hydrogen with the two-peak spectra resulting from coverage dependent reversible surface reconstruction.[11,12] Desorption of molecular nitrogen is observed above 900 K from atom recombination.[13] No residual nitrogen is detectable with Auger electron

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(1) (a) Ko, E. I.; Madix, R. J. *J. Phys. Chem.* **1981**, *85*, 4019. (b) Ko, E. I.; Benziger, J. B.; Madix, R. J. *J. Catal.* **1980**, *62*, 264.

(2) Pearlstine, K. A.; Friend, C. M. *J. Am. Chem. Soc.*, preceeding paper in this issue.

(3) Kemball, C.; Moss, R. L. *Proc. R. Soc. London, A* **1956**, *238*, 107.

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(7) Grunze, M.; Brundle, C. R.; Tomanek, D. *Surf. Sci.* **1982**, *119*, 133.

(8) Egawa, C.; Shindo, H.; Onishi, T.; Tamaru, K. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 927.

(9) Reed, A. P. C.; Lambert, R. M. *J. Phys. Chem.* **1984**, *88*, 1954.

(10) A broad range mass spectral desorption experiment was performed to search for reaction products: masses 2 through 90 were monitored. See: Liu, A. C.; Friend, C. M. *Rev. Sci. Instrum.*, in press.

(11) The desorption energetics of molecular hydrogen from atom recombination on W(100) are coverage dependent resulting from a reversible surface reconstruction.[12] The multiple peak spectrum observed for low $(CH_3)NH_2$ exposures is similar to that obtained for hydrogen atom recombination on clean W(100).[12] The presence of carbon and nitrogen on the surface may alter the expected desorption spectrum associated with the reconstruction, however.

(12) Horlacher Smith, A.; Chung, J. W.; Estrup, P. J. *J. Vac. Sci. Techol. A* **1984**, *2*, 877.

(13) Clavenna, L. R.; Schmidt, L. D. *Surf. Sci.* **1970**, *22*, 365.

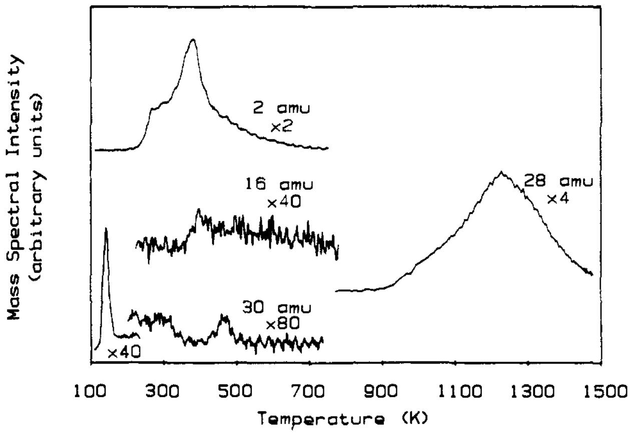

Figure 2. Thermal reaction of $(CH_3)_3N$ on W(100). Trimethylamine (30 amu), CH_4 (16 amu), H_2 (2 amu), and N_2 (28 amu) are produced. The initial dose in the experiment was 3.0 L at 120 K. Masses 58 and 31 were used to distinguish $(CH_3)_3N$ from $(CH_3)NH_2$. Refer to Table I for relevant mass spectral data.

spectroscopy subsequent to heating of the methylamine overlayer on W(100) to 1500 K in a temperature-programmed reaction experiment; only residual carbon remained.

Above 0.75 L of exposure, desorption of molecular methylamine commences (Figure 1). Desorption is observed in the range of 150–350 K. A desorption centered at 325 K corresponding to an approximate desorption energy of 19 kcal/mol is observed initially with a broad desorption over the range of 200–300 K appearing as the methylamine exposure is increased. Exposures above 1.5 L result in amine desorption at 150 K. This low-temperature desorption is attributed to sublimation of multiple layers of methylamine. Trace amounts of NH_3 are produced from reaction of methylamine on W(100) at 425 K for exposure greater than 1.0 L. Ammonia itself molecularly desorbs at 390 K from W(100).[16]

Trimethylamine on W(100). Thermal reaction of trimethylamine, $(CH_3)_3N$, on W(100) results in desorption of trimethylamine, methane, molecular hydrogen, and nitrogen as shown in Figure 2. No other volatile species are observed;[10] notably NH_3, HCN, and higher molecular weight amines are absent. Trimethylamine is distinguished from other amines on the basis of the ratio of intensities of 58 amu:30 amu in the data (Table I).

As in the case of $(CH_3)NH_2$, trimethylamine undergoes complete irreversible decomposition for exposures lower than 0.25 L. Only gaseous molecular hydrogen and nitrogen are produced from this reaction in desorption limited peaks as in the case of monomethylamine. The absolute amount of N_2 produced from decomposition of $(CH_3)_3N$ is approximately one-third the quantity from CH_3NH_2 decomposition at reaction saturation. Likewise, the relative amount of molecular hydrogen produced is approximately 3:5 from $(CH_3)_3N$ vs. CH_3NH_2 decomposition. (See Figures 1 and 2.) These observations are consistent with a fixed total amount of atomic nitrogen and carbon being accommodated by the W(100) surface prior to passivation. The measured ratios are the same as those prediced from the stoichiometry of $(CH_3)_3N$ vs. CH_3NH_2 assuming a fixed final carbon + nitrogen atom coverage from complete decomposition.

Desorption of trimethylamine itself is observed sequentially at 475, 310, 225, and 150 K for exposures greater than 0.3, 0.4, 0.5, and 2.5 L, respectively. The highest temperature amine desorption corresponds to a desorption energy of $\approx$28 kcal/mol.[15] The 150 K desorption does not saturate and is attributed to sublimation of condensed $(CH_3)_3N$. In addition, a trace amount of CH_4 is formed at 390 K for trimethylamine exposures greater than 1.0 L. Assuming pseudo-first-order kinetics, the activation energy for methane production is $\approx$23 kcal/mol.[15]

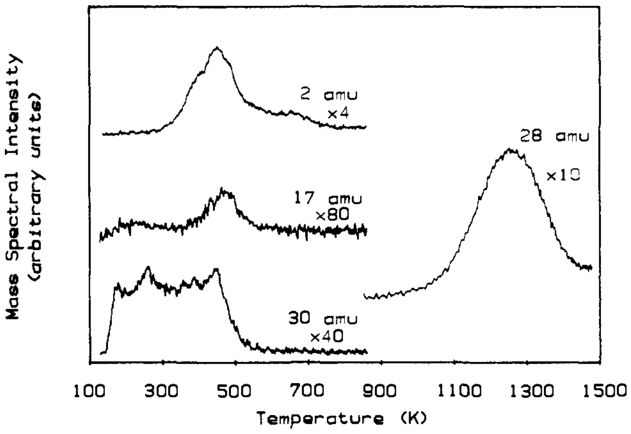

Figure 3. Thermal desorption data obtained for $(CH_3)NH_2$ adsorbed on W(100)-(5×1)-C: initial adsorption of a 3.3-L dose was effected at a crystal temperature of 120 K. $(CH_3)NH_2$ (30 amu), NH_3 (17 amu), H_2 (2 amu), and N_2 (28 amu) were produced. Other ions were monitored to establish the identity of the 30-amu peak as attributable to $(CH_3)NH_2$ (Table I).

Methylamine on W(100)-(5×1)-C. Methylamine undergoes competing thermal desorption and reaction on W(100)-(5×1)-C, as shown in Figure 3. The only volatile species detected are methylamine, ammonia, molecular hydrogen, and nitrogen. No other products are observed;[10] in particular, no CH_4 or higher molecular weight amines are produced.

As on the clean surface, irreversible decomposition predominates below 0.25 L on the -(5×1)-C surface. However, the energetics of irreversible decomposition are significantly different on the carbide with molecular hydrogen desorbing in a reaction limited peak at 490 K on the carbide.[14] In comparison, $(CH_3)NH_2$ decompositon occurs below 300 K on W(100). These decomposition temperatures correspond to estimated activation energies of 17 and 29 kcal/mol on W(100) and W(100)-(5×1)-C, respectively, assuming first-order kinetics and a preexponential factor of 10^{13} s^{-1}.[15] Molecular nitrogen is produced from atom recombination on the surface above 1100 K. No residual nitrogen is detectable with Auger electron spectroscopy, and the -(5×1)-C diffraction pattern is regenerated after flashing the surface with the methylamine overlayer to 1500 K. Additional carbon is evident on the surface subsequent to the temperature-programmed reaction experiment in the Auger spectrum. The extent of irreversible decomposition is maximum at an exposure of 0.45 L of methylamine, beyond which only increased molecular desorption is observed. The total amount of methylamine decomposition at saturation is approximately one-fourth that observed on initially clean W(100), as determined from the integrated areas of the N_2 and H_2 desorption features. The chemistry of the surface subsequent to removal of all nitrogen is essentially identical with the original -(5×1)-C.

Methylamine desorption commences at an exposure of 0.25 L with the maximum centered at 475 K. Higher methylamine exposures result in $(CH_3)NH_2$ desorption sequentially at 375, 250, and 170 K for exposures greater than 0.45, 0.9, and 1.0 L, respectively. At saturation, the parent desorption is essentially continuous as a function of temperature up to 525 K. Ammonia production is also observed in this temperature regime for methylamine exposures above 0.45 L. Trace amounts of ammonia production are reaction limited in this case: the maximum temperature NH_3 desorption for ammonia adsorbed on W(100)-(5×1)-C is 450 K.[16] All data are consistent with molecular amine adsorption followed by competing desorption and surface reaction near 475 K.

Trimethylamine on W(100)-(5×1)-C. Temperature-programmed reaction data obtained from reaction of trimethylamine

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(14) Desorption limited hydrogen production from atom recombination on W(100)-(5×1)-C is observed at 390 K.[7]

(15) (a) King, D. A. *Surf. Sci.* **1975**, *47* 384. (b) Although the assumption of a preexponential of 10^{13} s^{-1} may be incorrect, the preexponential for related molecules is expected to be approximately the same. Therefore, the observed differences may be attributed to relative energetics.

(16) Pearlstine, K. A.; Friend, C. M., unpublished data.

(17) Pearlstine, K. A.; Friend, C. M. *J. Phys. Chem.*, in press.

(18) Kemball, C.; Moss, R. L. *Proc. R. Soc. London, A* **1958**, *244*, 398.

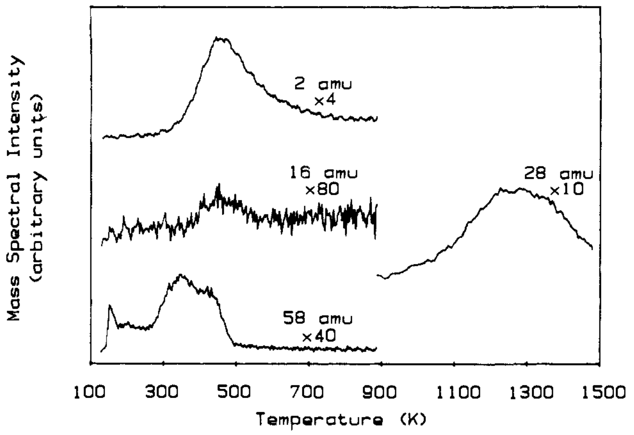

Figure 4. Reaction of $(CH_3)_3N$ on W(100)-(5×1)-C yields $(CH_3)_3N$ (58 amu), CH_4 (16 amu), H_2 (2 amu), and N_2 (28 amu). The dose used to generate the data shown was 2.5 L with the crystal maintained at 120 K.

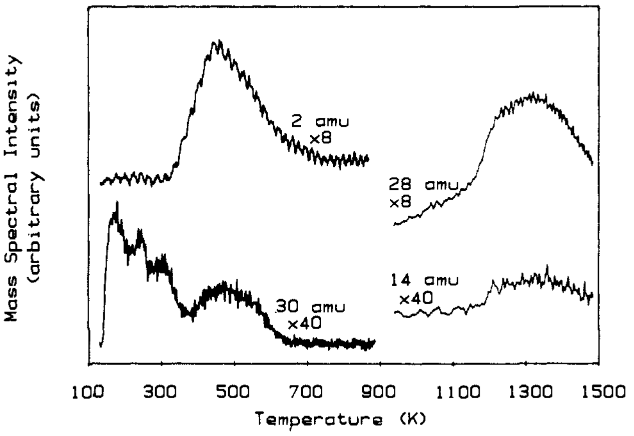

Figure 5. Methylamine desorption data subsequent to a 3.3-L dose at 120 K on W(100)-(2×1)-O. Methylamine (30 amu), H_2 (2 amu), N_2 (14 amu), and CO (12 amu) are produced. Data, not depicted, were obtained for other ions to establish 30 amu as being solely the result of methylamine desorption (Table I).

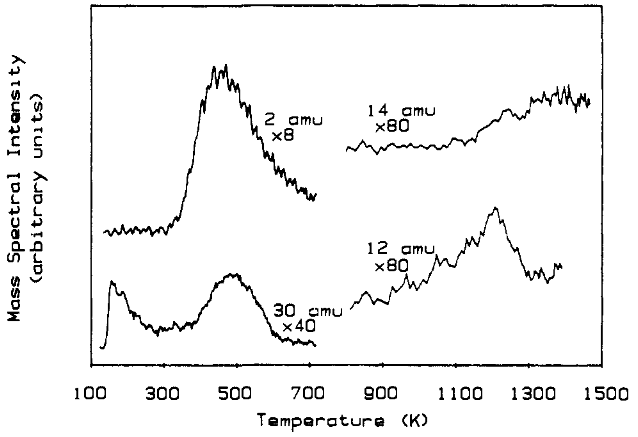

Figure 6. Thermal reaction of a 3.3-L dose of $(CH_3)_3N$ on W(100)-(2×1)-O. Trimethylamine (30 amu), H_2 (2 amu), N_2 (28 amu and 14 amu), and CO (28 amu) were detected.

on the W(100)-(5×1)-C surface are represented in Figure 4. Molecular trimethylamine, methane, H_2, and N_2 were the only desorbed species:[10] most notable is the absence of NH_3 formation.

Irreversible decomposition to form molecular hydrogen and nitrogen in desorption limited peaks centered at 390 K and above 1100 K, respectively. The total amount of irreversible decomposition of trimethylamine at reaction saturation is approximately one-half that on initially clean W(100), as measured from the H_2 and N_2 integrated intensities (Figures 2 and 4). The ratio of the H_2 and N_2 desorption intensities is measured as approximately 1:1 and 2:1, respectively, for decomposition of methylamine vs. trimethylamine on the -(5×1)-C. Larger $(CH_3)_3N$ exposures result in trimethylamine desorption at 450, 350, and 150 K above 0.5, 1.0, and 2.0 L, respectively. The 150 K peak does not saturate and is attributed to sublimation of condensed trimethylamine. Methane production, coincident with the highest temperature molecular peak at 450 K, appears above a trimethylamine exposure of 1.0 L. The -(5×1)-LEED pattern remained intact, and no nitrogen remained on the surface, as determined by Auger electron spectroscopy, subsequent to flashing to 1500 K. The chemistry associated with the -(5×1)-C was also essentially identical with the freshly prepared carbide subsequent to amine reaction and flashing to desorb all nitrogen.

Methylamine on W(100)-(2×1)-O. Thermal treatment of a methylamine overlayer results in desorption of H_2, N_2, and CO as shown in Figure 5. No other desorption products were observed under the conditions of this experiment.[10]

In contrast to the W(100) and W(100)-(5×1)-C surfaces, molecular desorption of methylamine is observed even for exposures less than 0.10 L, at 500 K, i.e., $E_d \approx 30$ kcal/mol with very little accompanying irreversible decomposition. Higher exposures result in an increase in the amount of methylamine desorption at temperatures below 500 K. At 3.3 L of exposure, essentially continuous desorption of the amine is observed in the temperature regime of 150-500 K. The detailed nature of the poorly resolved desorption features was not investigated further. Desorption of molecular hydrogen is observed initially at ≈500 K for methylamine exposures of 0.3 L. The H_2 desorption feature increases in intensity with unresolved features filling in at lower temperature as the exposure is increased with the onset of molecular hydrogen desorption occurring at 350 K for an ethylamine exposure of 3.3 L (Figure 5). The total amount of decomposition at reaction saturation is approximately one-fourth that obtained on initially clean W(100) based on the N_2 integrated intensity. Both CO and N_2 are formed via atom recombination above 1100 K in limited quantities. The activation energy for methylamine decomposition on the -(2×1)-O surface is higher than on W(100) as indicated by the limited amount of dehydrogenation, the high temperature (>500 K) at which molecular desorption is observed, and the fact that reversible molecular desorption occurs even at low exposures.

Trimethylamine on W(100)-(2×1)-O. As in the case of monomethylamine, trimethylamine primarily undergoes reversible desorption with some accompanying decomposition. As shown in Figure 6, only trimethylamine, molecular hydrogen, CO and N_2 were observed in the desorption spectra.[10] Initially, trimethylamine desorption is observed at 500 K with higher exposures resulting in a shift to lower temperature in the range of 120 to 600 K. Desorption of molecular hydrogen occurs in the range of 300-700 K at saturation. Both CO and N_2 are formed via atom recombination at 1200 K and greater than 1300 K, respectively. The amount of H_2 produced is approximately the same as from the methylamine reaction on the -(2×1)-O surface with N_2 being smaller by roughly a factor of 2.

As in the case of the monomethylamine, trimethylamine appears to be stabilized with respect to irreversible decomposition on W(100)-(2×1)-O compared to W(100). The trimethylamine is also strongly bound to the -(2×1)-O with the highest temperature molecular desorption corresponding to a desorption energy of 39 kcal/mol. This does not, however, permit C-N bond activation to yield CH_4 or NH_3.

Discussion

The reactivity and selectivity associated with methyl- and trimethylamine on W(100) are dependent both on the presence of adlayers of carbon or oxygen and the degree of amine substitution. The W(100)-(5×1)-C[19-21] and W(100)-(2×1)-O[22-25]

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(19) Benziger, J. B.; Ko, E. I.; Madix, R. J. *J. Catal.* **1978**, *54*, 414.

(20) Rawlings, K. J.; Toulias, S. D.; Hopkins, B. J. *J. Phys. C: Solid State* **1981**, *14*, 5411.

(21) Stefan, P. M.; Spicer, W. E. *Surf. Sci.* **1985**, *149*, 423.

Table II. Maximum Temperature Molecular Desorption[a] at Saturation and Corresponding Desorption Energies

	molecule					
surface	NH_3[16]	(E_d, kcal/mol)	CH_3NH_2	(E_d, kcal/mol)	$(CH_3)_3N$	(E_d, kcal/mol)
W(100)	390 K	(23)	330 K	(19)	475 K[b]	(28)
W(100)-(5×1)-C	460 K	(27)	475 K	(28)	475 K	(28)
W(100)-(2×1)-O	600 K	(35)	600 K	(35)	650 K	(39)

[a] These treatments reflect the point where the desorption intensity decreases to one-half the highest temperature maximum. [b] The character of the trimethylamine desorption on W(100) differs from all other spectra in that the highest temperature desorption is discrete. A broad desorption is observed between 150 and 330 K which is analogous to the other cases cited.

surfaces have been studied extensively previously. Both were altered in both geometric and electronic structure with respect to clean W(100). The -(5×1)-C surface is proposed to be a good model for the basal plane of WC. Energy dependent photoemission studies support this contention.[21] The -(2×1)-O does not approach bulk WO_3 in geometric or electronic structure, but it is proposed to incorporate oxygen to some extent below the topmost tungsten layer and renders surface tungsten atoms quite electron deficient based on the chemical shift of the $W_{4f_{7/2}}$ B.E. by 0.8 eV.[25]

The most striking feature of the chemistry of both the mono- and trisubstituted amine is the smaller extent of irreversible decomposition on the -(5×1)-C and -(2×1)-O surfaces compared to W(100). Ammonia,[16] methylamine, and trimethylamine all behave similarly on a given surface as is evident from the data presented in Table II. All three molecules undergo limited amounts of decomposition with molecular desorption being observed up to 600 and 650 K for NH_3, $(CH_3)_3N$, and $(CH_3)NH_2$, respectively, on the -(2×1)-O surface. This observed stabilization with respect to dehydrogenation on the -(2×1)-O has also been observed for ethylamine.[2] The onset of irreversible decomposition on W(100)-(5×1)-C is 400 K in all three cases, corresponding to an activation energy for decomposition of ≈24 kcal/mol. The energetics for decomposition are lowest on W(100) as evidenced by the desorption of molecular hydrogen below 300 K setting an upper limit for the activation energy for decomposition of 17 kcal/mol, assuming first-order kinetics and a preexponential of 10^{13} s^{-1}.[15] Analogous differences between the -(5×1)-C and W(100) have been observed for HCN. The trend in adsorption strengths is consistent with the most electron deficient surface, i.e., the -(2×1)-O, interacting most strongly with the amine, a good electron donor. The relative facility of dehydrogenation on the three surfaces may actually be related to the adsorption properties of atomic C, N, and H, given the generality of the observed trend for different classes of molecules. Comparison of the relative amount of decomposition for methylamine vs. trimethylamine on the carbide and oxide surface suggests that a fixed amount of atomic hydrogen is accommodated by the two modified surfaces. Alternatively, all three surfaces may accommodate a fixed amount of carbon plus nitrogen, thus, dictating the extent of decomposition. Initial decomposition, however, is expected to involve C-H bond scission. Therefore, the ability of the modified surfaces to adsorb hydrogen atoms must play a role in the amine chemistry. Previous investigations have shown that the saturation coverage for atomic hydrogen is smaller by a factor of 5 on the -(5×1)-C compared to clean W(100),[19] consistent with the observed trend in reactivity. Further, the fact that a similar trend in reactivity is observed for different classes of molecules supports the contention that changes in atomic adsorption dictate the alteration in chemistry. It is interesting to note that the trend in the activation energy for dehydrogenation increasing as the surface is rendered more electron deficient is consistent with theoretical investigations of CH_4 activation on Ni(111) which proposed that donation of electron density from the surface to C-H σ^* orbitals leads to C-H bond activation.[28] Thus, electron deficient surfaces, which are poorer electron donors, will be less effective in activating C-H bonds. Likewise, donation of electron density from the surface to the σ^* orbital of molecular hydrogen as been implicated in H_2 dissociation.[28] This is consistent with the observation of a low H_2 dissociation probability on the carbide and oxide surfaces,[1] presumably due to a barrier to dissociation.

Alterations in reactivity and selectivity are also observed that are consistent with the trends in stabilization on the three surfaces investigated. Carbon-nitrogen bond activation and hydrogenation result in methane production from trimethylamine on "passivated" W(100) and W(100)-(5×1)-C in the range of 400-600 and at 475 K, respectively. In contrast, no CH_4 formation is evident from methylamine reaction on either W(100) or the -(5×1)-C: rather, ammonia is produced. This result is analogous to that obtained for the ethyl analogues where reaction of triethylamine yields C_2H_4 whereas monoethylamine produces NH_3.[2] No C-N bond scission products are observed on W(100)-(2×1)-O from either molecule, consistent with the overall decrease in decomposition compared to W(100) and W(100)-(5×1)-C. The temperatures at which CH_4 and NH_3 are formed from $(CH_3)_3N$ and $(CH_3)NH_2$, respectively, are essentially the same on W(100) and W(100)-(5×1)-C. This observation and the fact that C-N bond cleavage products are only formed subsequent to substantial decomposition on W(100) supports the idea that these reactions are occurring on a surface passivated with carbon and nitrogen which exhibits reactivity similar to the -(5×1)-C.

The most significant difference in the chemistry of the methylamine vs. ethylamine is the absence of nitrile formation. Ethyl- and triethylamine react to form acetonitrile on W(100) and W(100)-(5×1)-C,[2] while no HCN formation is detected from reaction of their methyl analogues. On W(100), HCN itself primarily undergoes irreversible decomposition[19] which renders observation of gaseous HCN unlikely if formed on the surface. However, adsorbed HCN is reversibly desorbed to a large extent on W(100)-(5×1)-C[17] and W(100)-(2×1)-O. Therefore, the absence of HCN desorption from reaction of methyl or trimethylamine on the -(5×1)-C surface precludes its formation. These data are analogous to those in previously reported studies of $(CH_3)NH_2$[3] and $C_2H_5NH_2$[17] reactions on evaporated films. Methylamine did not form any HCN whereas ethylamine primarily yielded CH_3CN. These data were interpreted as resulting from rapid hydrogen interchange between the amine and the surface with C-N bond scission being the rate limiting step for hydrogenolysis. The activation energy for methylamine decomposition on evaporated tungsten was reported to be 17.0 kcal/mol in the range of 493-553 K,[3] the same magnitude estimated for $(CH_3)NH_2$ decomposition on W(100).

Surprisingly, there are considerable differences in the product distribution and reactivity associated with Mo(100) and oxidized Mo(100) compared to the W(100)-based surfaces.[6] On Mo(100), HCN and CH_4 were reported as major reaction products from trimethylamine with no molecular desorption and limited amounts of molecular hydrogen desorption above 440 K. These data suggest a large difference in the energetics for irreversible C-H vs. C-N bond scission on W(100) compared to Mo(100).

The changes in chemistry associated with methylamine induced by the -(5×1)-C are analogous to previous studies of methanol on W(100) and W(100)-(5×1)-C.[1] On clean W(100), methanol

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initially irreversibly decomposed to atomic C, O, and H at 300 K. Higher exposures result in formation of surface methoxy which undergoes several competing processes: methane formation, H_2CO production, decomposition to yield CO and H_2, and regeneration of methanol. As in this study, initial decomposition of methanol was proposed to result in "passivation" of the W(100) surface. On the -(5×1)-C surface, a larger fraction of the methanol reversibly desorbs below 400 K, reflecting a reduced amount of irreversible decomposition compared to the clean surface. Surface methoxy is formed via O-H bond scission which further reacts to yield CH_4, CH_3OH, H_2CO, $HCOOCH_3$, CO, H_2, CO_2, and H_2O. In the case of methanol, products resulting from both C-O and C-H bond scission are observed. The fact that H_2CO is observed from methanol reaction while HCN is not observed from reactions of $(CH_3)NH_2$ or $(CH_3)_3N$ is a rather surprising contrast. This may be the result of differences in adsorption structure of the two molecules or differences in the lability of C-H bonds. Alternatively, the fact that HCN formation requires scission of two N-H or C-N bonds and two C-H bonds whereas only one O-H and one C-H bond must be cleaved in order to form H_2CO from methanol may account for this discrepancy. It is interesting to note that the energetics of methoxy reaction are essentially the same on the -(5×1)-C vs. W(100) surfaces, analogous to the similar energetics observed for NH_3 and CH_4 formation from the amines. Further, the reactivity and selectivity for methanol were reported to be essentially the same on clean and modified Mo(100) as their W(100) analogues,[27] in contrast to the reported differences in amine reactivity on Mo(100)[6] vs. W(100).

Conclusions

The reactivity and selectivity associated with methyl- and trimethylamine on W(100), W(100-(5×1)-C, and W(100)-(2×1)-O surfaces are dependent on the presence of adlayers and the extent of amine substition. The stability of both amines and ammonia with respect to irreversible decomposition is greatly enhanced on the -(2×1)-O and -(5×1)-C compared to W(100). The generality of this trend suggests that the extent and energetics of both N-H and C-H bond activation are altered by the presence of the oxide and carbide layer and may result from the adsorption energetics and the ability to accommodate adatoms on modified surfaces.

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Stable Ylides H_2CClH, H_2CFH, H_2COH_2, and H_2CNH_3 Studied by Neutralization-Reionization Mass Spectrometry

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Abstract: Contrary to the predictions of ab initio theory, the neutral ylides H_2CClH (**1**), H_2CFH, and H_2COH_2, as well as H_2CNH_3, exist in local energy minima. These have been prepared for study from fast gaseous $H_2CYH^{\cdot+}$ ions by neutralization with Hg vapor. Reionization of the resulting fast neutrals produces abundant molecular ions, which could represent $H_2CYH^{\cdot+}$ or $H_3CY^{\cdot+}$ from partial or complete isomerization of H_2CYH to the more stable isomer H_3CY. However, increasing the pressure of the reionizing collision gas (O_2 or He) increases the relative abundance of YH dissociation products, such as HCl from **1**, which must originate from H_2CYH, not H_3CY. Thus an appreciable fraction of each of these neutral ylides must have survived for the microsecond lifetime of the experiment. For **1** this was confirmed by reionization to H_2CClH^{2+}, which shows a significantly different fragmentation pattern from that obtained from H_3CCl. More than half of **1** molecules formed by vertical neutralization are still undissociated after 10^{-6} s, and of these less than half have isomerized to H_3CCl. It appears that theory overestimates the heat-of-formation values for such hypervalent neutral species.

Ylides are widely utilized as intermediates in organic synthesis.[1] For these hypervalent species stable forms such as certain iodonium ylides ($R_2C^{-}—I^{+}R \leftrightarrow R_2C{=}IR$) are rare,[2] so that most characterizations of the structure and energetics of the simplest ylides H_2CYH have been based on molecular orbital theory.[3] In contrast, the ionized forms of many such simple ylides are actually more stable thermodynamically than their conventional isomers (e.g., $^{\cdot}CH_2O^{+}H_2$ vs. $H_3COH^{\cdot+}$); theoretical and experimental studies show that the ionic isomers are usually separated by high isomerization barriers.[4] Here we use neutralization[5,6] of the appropriate ylide ions to prepare several simple gaseous ylides (Y = Cl, **1**; F, **2**; OH, **3**; NH_2, **4**), studying these by collisionally activated dissociation (CAD) and reionization.[5]

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