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Alteration in Surface Reaction Selectivity of Nitriles. 2. CH_3CN on W(100) and W(100)-(5×1)-C

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The adsorption and reaction of acetonitrile has been investigated on clean W(100) and W(100)-(5×1)-C surfaces, using thermal desorption spectroscopy and isotopic labeling. Irreversible decomposition of acetonitrile dominates on clean W(100) producing gaseous N_2, H_2, and adsorbed carbon. At high acetonitrile exposures some molecular CH_3CN desorption is observed at 190 K as well as C–C bond activation and hydrogenation which results in CH_4 and HCN formation. The activation energy for irreversible decomposition of CH_3CN and the reaction selectivity are dramatically different on the -(5×1)-C surface, a model for the basal plane of WC(0001). In this case, the thermal desorption spectrum of the parent CH_3CN consists of five poorly resolved features with acetonitrile desorption observed up to 600 K. The acetonitrile peaks above 400 K on this surface are attributed to rehydrogenation of adsorbed CH_2CN. Molecular hydrogen, nitrogen, and hydrogen cyanide were the only additional reaction products detected. No methane formation was observed, indicating that C–C bond activation is less facile on the -(5×1)-C vs. clean W(100). The production of HCN is attributed to intramolecular hydrogen atom transfer of surface bound HCCN.

Introduction

Acetonitrile is a proposed surface intermediate from reaction of alkyl amines on transition-metal-based surfaces.[1,2] Thus, an understanding of the surface reactions that acetonitrile undergoes is important in both verifying its role as an intermediate and understanding the ultimate distribution or products obtained in amine reactions. In addition, several competing types of bond activation, C–C, C–H, and C–N, may occur in this molecule, rendering it possible to characterize selectivity changes induced by surface alteration.

Acetonitrile has been previously investigated on several late transition-metal surfaces, namely Ni(111), Ni(100), Ni(110), Ni[9(111)×(111)],[3] Pt(111),[4] Ag(110),[5] and polycrystalline Ni and Pd films.[6] On these surfaces, acetonitrile primarily exhibits reversible molecular adsorption with a minor amount of accompanying irreversible decomposition yielding gaseous H_2 and N_2. Spectroscopic investigations have identified both end-on bridge bonding[3,6] and side-on bonding[5] modes. Acetonitrile bonding and reactivity were found to be substantially altered by adsorbed oxygen on Ag(110).[5] Atomic oxygen stabilizes molecularly adsorbed CH_3CN via a Lewis acid–base interaction and induces reversible C–H bond scission to yield CH_2CN. Other reported studies have not established a precedent for alteration in acetonitrile chemistry induced by adatoms.[3]

This reported work is part of a series of studies aimed at characterizing alteration in surface reaction selectivity and reactivity on W(100) induced by the presence of electronegative adatoms. This investigation focuses on the reaction of acetonitrile on clean W(100) and W(100)-(5×1)-C surfaces. The stability of CH_3CN toward irreversible decomposition reactions is found to be greatly enhanced on the -(5×1)-C compared to the clean surface. In addition, the selectivity for C–H vs. C–C bond activation is significantly altered by the carbide overlayer. Analogous studies have been performed with HCN which exhibit similar alteration in the relative energetics and extent of C–H bond scission on the clean vs. carbide surface.

Experimental Section

All experiments described were performed in an ultrahigh vacuum system with a working base pressure of 2×10^{-10} torr, described previously.[7] The W(100) crystal was aligned (±0.5°) by Laue X-ray backdiffraction, cut by Spark erosion, and mechanically ground and polished. Cleaning in vacuo was performed by cycles of treatment in $\approx 1 \times 10^{-7}$ Torr pressure of $O_2(g)$ at a crystal temperature of 1400 K and subsequent flashing to 2500 K. The -(5×1)-C surface was prepared by exposure to 60 langmuirs of ethylene with the crystal maintained at $\approx$1500 K. Low-energy electron diffraction and Auger electron spectroscopy were used to determine surface order and cleanliness, respectively.

All acetonitrile was obtained commercially, dried over CaH_2, and degassed immediately prior to use; CH_3CN (Mallinckrodt Chemical Co., 99% purity), CD_3CN (MSD Isotopes, 99.7 atom % D), hydrogen (99.9995% purity), oxygen (extradry, 99.6% purity), and ethylene (99.5% purity) were all purchased from Matheson and used without further purification.

Dosing was performed with directed beam dosers which allowed maintenance of the chamber pressure below 2×10^{-9} Torr during adsorption, minimizing background reaction and pumpdowm time. Thermal desorption data were obtained with a quadrupole mass spectrometer in conjunction with an IBM-PC, using either radiative ($T_{max} < 1000$ K) or electron bombardment heating ($T_{max} \approx 1500$ K). The mass spectrometer was enclosed in a cryogenic shield equipped with a rotatable flag with an orifice of 0.0625-in. diameter. the crystal was positioned at 0.12 in. from the mass spectrometer orifice, resulting in selective detection of molecules desorbed directly from the crystal. This configuration precludes background reaction or desorption from contributing to the observed chemistry.

Results and Discussion

Clean W(100). Acetonitrile (CH_3CN) adsorbed on clean W(100) at 120 K yields molecular CH_3CN, methane, HCN, H_2, and N_2 as volatile reaction products as represented in Figure 1. Low exposures (<0.25 langmuir) of acetonitrile result in irreversible decomposition to yield gaseous molecular hydrogen and nitrogen in desorption limited peaks at 350 and >1100 K, respectively. Higher exposures (0.25–1.0 langmuir) result in additional desorption products: CH_3CN at 190 K, CH_4 at $\approx$420 K, and HCN at $\approx$650 K. The H_2 and N_2 desorption spectra also develop additional poorly resolved features above 450 and $\approx$1000 K, respectively, for acetonitrile exposures greater than 0.45 langmuir.

Exposures greater than 1.0 langmuir result in condensation of acetonitrile. Thermal treatment of acetonitrile multilayers (>1.0-langmuir exposure) induces sublimation of CH_3CN at 150 K (Figure 1) with no increase in the intensity of reaction products

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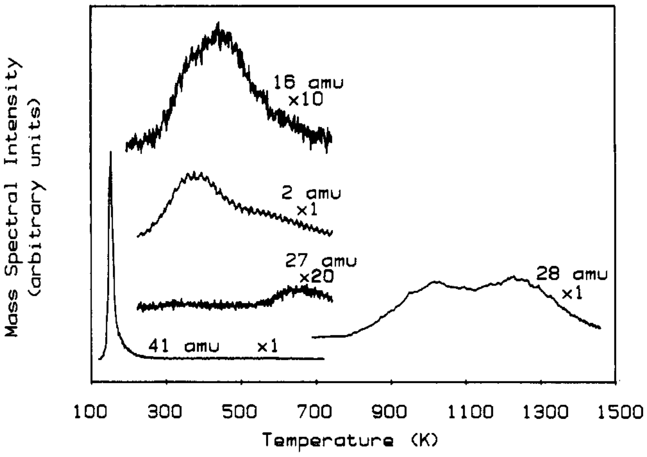

Figure 1. Desorption of acetonitrile (41 amu), hydrogen cyanide (27 amu), hydrogen (2 amu), methane (16 amu), and nitrogen (28 amu) from reaction of a 1.6-langmuir dose of acetonitrile on W(100). Acetonitrile is initially adsorbed at 120 K and thermally desorbed with a heating rate of 15 K s^{-1}. The nitrogen was desorbed by electron bombardment heating which results in a nonlinear heating rate of 20–40 K s^{-1}.

TABLE I: Methane Isotopes Produced from Reaction of Adsorbed Deuterium and CH_3CN on W(100)[a]

predominant ion	mass/charge	relative abundance[b]
CH_4^+	16	1.0
CH_3D^+	17	0.6
$CH_2D_2^+$	18	0.16
CD_3H^+	19	0.10
CD_4^+	20	0.0

[a] The H:D ratio desorbing from atom recombination on the surface is 1.0:0.8 in this experiient. [b] The given ratios are uncorrected for fragmentation in the mass spectrometer.

compared to monolayer coverages.

Coadsorption of atomic deuterium and CH_3CN on W(100)[9,10] results in deuterium incorporation into the methane formed with CH_4 and CH_3D being the primary isotopes and minor amounts of CH_2D_2 and CHD_3 observed (Table I). No incorporation of deuterium into CH_3CN or HCN was observed in these experiments.

These results suggest that at low exposures acetonitrile undergoes irreversible C–H bond scission prior to 350 K and C–C and C–N bond cleavage similar to that observed for HCN on W(100). These studies cannot, however, identify the temperature for these processes. At higher CH_3CN exposures, methane and HCN production and molecular acetonitrile desorption are observed. Methane is proposed to be produced primarily from hydrogenation of the methyl group of intact acetonitrile on the basis of the fact that the D + CH_3CN reaction yields CH_3D as the major product. An analogous reaction occurs for ethylamine on W(100).[2] The extent of surface deuterium incorporation into the methane formed from ethylamine is essentially identical with the acetonitrile case. In the case of ethylamine, reaction of $CH_3{}^{13}CH_2NH_2$ did not yield any detectable $^{13}CH_4$, confirming that only the methyl carbon leads to methane formation. This is used to support the contention that the methyl not cyano carbon is hydrogenated. It is also possible that adsorbed methyl groups are hydrogenated to yield methane. This is presumed to be less likely thermodynamically under ultrahigh vacuum conditions because dehydrogenation of methyl is expected to predominate on an active surface such as tungsten. This possibility cannot be ruled out on the basis of the available data, however, but must be verified spectroscopically. The production of CH_2D_2 and CH_3D is proposed to result from reversible H–D exchange into the methyl group prior to hydrogenation. HCN production is proposed to result from intramolecular hydrogen transfer to the CN group based on the fact that surface deuterium is not incorporated into the HCN. Initial decomposition of CH_3CN increases the coverage of adsorbed atomic hydrogen, necessary for hydrogenation reactions, and may also "passivate" the surface, such that irreversible C–H, C–C, and C–N bond cleavage is less facile, by forming an overlayer of C and N. This contention is based on the fact that the high coverage reactivity resembles the trend observed on the -(5×1)-C where reversible processes predominate.

TABLE II: Ratio of Desorbing Acetonitrile Isotopes after Adsorption of 4.0 langmuirs of a CH_3CN/CD_3CN Mixture on W(100)-(5×1)-C

	relative intensity[a]				
isotope	150 K	225 K	325 K	450 K	550 K
CD_3CN	1.0	1.0	1.0	1.0	1.0
CD_2HCN	0.0	0.07	0.07	0.55	0.95
CDH_2CN	0.0	0.05	0.05	0.54	0.93
CH_3CN	1.06	0.81	0.77	1.53	2.22

[a] The relative intensities are normalized in each peak to the CD_3CN intensity and corrected for fragmentation in the mass spectrometry.[19]

TABLE III: Relative Intensity of Desorption at 325 K vs. 450 K for Acetonitrile Reaction on W(100)-(5×1)-C

adsorbate	44 amu	41 amu
CD_3CN	1.5:1	
CH_3CN		1.4:1
CD_3CN + CH_3CN	3:1	1.2:1

W(100)-(5×1)-C: The W(100)-(5×1)-C surface, described previously,[11-13] is considered a good model for the basal plane of bulk WC, having similar electronic and geometric structures. The proposed structure of the -(5×1)-C consists of an hexagonal arrangement of tungsten atoms in the topmost layer with all carbon atoms lying below the surface plane. This structure allows modification of the tungsten surface geometric and electronic structure without directly blocking surface sites.

As in the case of hydrogen cyanide,[8] reaction selectivity and stability with respect to irreversible bond cleavage of acetonitrile is dramatically different on the -(5×1)-C compared to the clean W(100) surface. The volatile thermal reaction products observed from a high coverage CH_3CN overlayer on W(100)-(5×1)-C are acetonitrile, HCN, H_2, and N_2, as shown in Figure 2.[14] No methane was produced from acetonitrile reaction on the -(5×1)-C in sharp contrast to the clean surface case.

The desorption spectrum of parent acetonitrile at high exposures consists of six poorly resolved features centered approximately at 150, 225, 325, 450, 550, and 675 K.[15] The 450 K desorption appears first as a function of acetonitrile exposure (<0.3 langmuir) with the 325, 550, 225, and 150 K peaks appearing sequentially as a function of CH_3CN exposure. The 150 K desorption feature is relatively sharp and continuously increases in intensity as a function of acetonitrile exposure. This behavior is typical for sublimation of CH_3CN multilayers. All other 41-amu desorption peaks saturate at an exposure of 1.7 langmuirs.

At exposures of <0.3 langmuir CH_3CN undergoes competing desorption at 450 K and irreversible decomposition to produce gaseous H_2 in a broad temperature regime (400–750 K) and gaseous N_2 above 1100 K. Above 0.3-langmuir acetonitrile ex-

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(9) The presence of atomic hydrogen is known to induce reconstruction of the W(100) surface.[10] There is no evidence for alteration in the observed chemistry in these studies in that the desorption data obtained with and without deuterium preadsorption are essentially identical.

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(14) No other desorption products were observed. Masses 16–18, 22, 30, 41, 42, 52, and 56 were specifically monitored in addition to the reported desorption spectra.

(15) The poor resolution is not due to background desorption or reaction. As described the features appear sequentially as a function of initial acetonitrile exposure. The breadth of some of the peaks may be due to hydrogen bonding of acetonitrile, which is known to occur in solid CH_3CN.[16]

posures, desorption of the parent near 325 K appears. This desorption peak is unusually broad and appears to shift to lower temperature with increasing coverage. At exposures of greater than 0.9 langmuir, the 550 and 675 K CH_3CN desorption peak appears with accompanying HCN and increasing gaseous H_2 desorption centered at 675 K. The HCN desorption is reaction limited; HCN itself desorbs at 450 and 650 K on the -(5×1)-C surface.[8]

Reaction of a 1:1 mixture CH_3CN and CD_3CN on the -(5×1)-C surface results in H–D exchange in the 450 and 550 K desorption peaks and an isotope effect in the selectivity of desorption vs. surface reaction in the 200–400 K temperature range. The mass spectral data for the CH_3CN/CD_3CN coadsorption experiment are summarized in Table II.

The relative amount of acetonitrile desorption in the temperature range of 200–350 K, where no significant H–D exchange is evident in the mixing experiment, compared to the 400–600 K regime, where H–D exchange prevails, exhibits a kinetic isotope effect. The isotope effect is evident from inspection of the data presented in Tables II and III: a larger fraction of CD_3CN relative to CH_3CN desorbs at 225 and 325 K compared to the initial mixture and 150 K sublimation peak. The two high-temperature peaks at 450 and 550 K exhibit H–D exchange and a smaller relative amount of CD_3CN desorption. No shifts in desorption peak temperatures are evident for the different acetonitrile isotopes. An analogous effect is not observed when pure CH_3CN or CD_3CN is adsorbed on the -(5×1)-C (Table III). The relative amount of desorption at 325 K vs. 450 K is 1.5:1 and 1.4:1 for CH_3CN and CD_3CN, respectively, when solely adsorbed. In contrast, the relative intensities at 325 K vs. 450 K for CH_3CN and CD_3CN are 3:1 and 1.2:1, respectively, for a 1:1 mixture.

The data presented are consistent with competing molecular desorption, reversible C–H bond activation, and some irreversible decomposition. A proposed mechanism for CH_3CN reaction on W(100)-(5×1)-C is outlined eq 1–8.

$$CH_3CN(g) \rightleftharpoons CH_3CN(a) \quad (1)$$

$$CH_3CN(a) \rightleftharpoons CH_2CN(a) + H(a) \quad (2)$$

$$CH_2CN(a) \rightleftharpoons CHCN(a) + H(a) \quad (3)$$

$$CHCN(a) \rightleftharpoons HCN(g) + C(a) \quad (4)$$

$$CHCN(a) \rightleftharpoons CN(a) + C(a) + H(a) \quad (5)$$

$$2H(a) \rightleftharpoons H_2(g) \quad (6)$$

$$CN(a) \rightleftharpoons C(a) + N(a) \quad (7)$$

$$2N(a) \rightleftharpoons N_2(g) \quad (8)$$

Stepwise reversible C–H bond cleavage, steps 2 and 3, is proposed to compete with reversible molecular desorption, step 1, in order to account for the observed H–D exchange in the 450 and 550 K nitrile desorption peaks.[25] The estimated isotopic ratios of CH_3CN, CH_2DCN, and CHD_2CN relative to CD_3CN are 2.0, 1.4, and 1.4, respectively, assuming that the nitrile is regenerated solely from hydrogenation of CH_2CN or CD_2CN, the reverse of step 2. This estimate neglects an isotope effect for the probability of CH_2CN compared to CD_2CN hydrogenation[21] and assumes that the ratio of $CH_2CN:CD_2CN$ = H:D = 1.0:0.7. The calculated ratios are in reasonable agreement with the exchange data obtained in the 550 K peak (Table II).

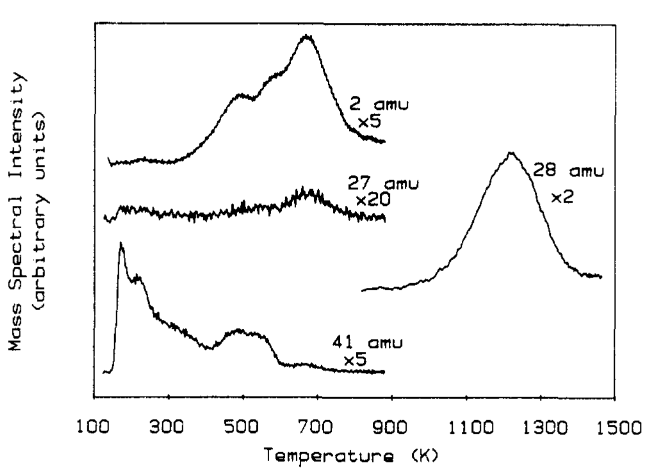

Figure 2. Desorption of acetonitrile (41 amu), hydrogen cyanide (27 amu), hydrogen (2 amu), and nitrogen (28 amu) from reaction of a 2.2-langmuir dose of CH_3CN on W(100)-(5×1)-C. The heating rate was 15 K s^{-1} for the low-temperature desorptions and 30 K s^{-1} for the nitrogen desorption.

In order to explain the fact that an isotope effect is observed in the mixture but not in overlayers of pure CH_3CN or CD_3CN, partial dehydrogenation must compete with molecular adsorption, steps 1 and 2 at low temperature. The exchange data (Table II) was obtained for exposures where all peaks originating from surface reaction are saturated. The results are accounted for by assuming that there are a fixed number of sites available for adsorption of atomic hydrogen or deuterium and that quasiequilibrium exists throughout the desorption experiment. This leads to the same amount of CH_2CN vs. CD_2CN formed on the surface at low temperature in the pure overlayers. Adsorption of the mixture on the -(5×1)-C is a competition reaction between CH_3CN and CD_3CN. Given that the activation energy for C–D bond scission is greater than for C–H bond scission because of the lower zero point energy of a C–D bond, competition between CH_3CN and CD_3CN will result in a larger extent of partial dehydrogenation of the perhydrido compared to the perdeuterio isotope in the mixture. This accounts for the observed isotope effect in the mixture and the absence of an isotope effect in comparing pure CD_3CN to pure CH_3CN. Thus, the concentrations of CD_2CN and D are lower than CH_2CN and H in the exchange experiment. This assertion is confirmed by a higher relative amount of atomic hydrogen compared to deuterium in the exchange experiment. A 1:1 mixture of CH_3CN and CD_3CN results in a ratio of H:D of approximately 1.0:0.7, as measured from integrated thermal desorption intensities of molecular hydrogen isotopes.

Irreversible decomposition competes with rehydrogenation in the proposed mechanism. Steps 3–5 in the mechanism are predicated on the multiple peak structure of reaction-limited molecular hydrogen production (Figure 2). The poorly resolved peaks at 500 and 675 K are attributed to dehydrogenation of CH_2CN and CHCN, respectively. The coincidence of the 675 K H_2 feature and reaction-limited HCN production[2] gives evidence for decomposition of a common intermediate at this temperature, proposed to be CHCN as outlined in steps 4 and 5 in the mechanism. Intramolecular hydrogen transfer to the cyano group in CHCN is invoked.

Carbon–nitrogen bond activation is proposed to precede molecular nitrogen formation. This contention is based on the fact that the N_2 desorption spectrum is analogous to that obtained from atom recombination on W(100)-(5×1)-C.[22] This, however, is not central to the selectivity and reversibility in C–H bond activation. The most remarkable aspect of the chemistry of acetonitrile on W(100)-(5×1)-C is the increased stability of hydrogen-containing fragments with respect to irreversible decomposition in contrast to W(100) where dehydrogenation is complete prior

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(19) Intensities were measured by using the peak height at a specific temperature in the desorption spectrum. The ratio of the parent ion to that for loss of one hydrogen (deuterium) atom is 10:6 in gaseous acetonitrile at 300 K. Corrections were made to the mass 43, 42, and 41 signals by assuming the same degree of fragmentation in the desorption spectra to yield the reported ratios. This assumption may give rise to some error in that fragmentation patterns have been shown to be temperature dependent in some cases.[20] This would not, however, change the qualitative result.

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to 500 K. An analogous increase in stability with respect to irreversible dehydrogenation on the -(5-1)-C vs. W(100) surface was observed for HCN.[8] This suggests a general trend in limiting irreversible decomposition of nitriles as a result of dehydrogenation, not specifically related to the presence of methyl hydrogens. It is possible that the differences in extent and energetics of C–H bond activation are the result of differences in the energetics and saturation coverage of atomically adsorbed hydrogen on W(100) vs. W(100)-(5×1)-C. An analogous argument was made for methanol reaction on these two surfaces.[23] This is also supported by the generality in alteration of C–H bond scission on the two surfaces; alkyl alcohols,[23] amines,[2] and nitriles all behave similarly. The generality of the observed trend in reactivity for different classes of molecules suggests that differences in the adsorption properties of atoms on the W(100) and W(100)-(5×1)-C surfaces dictate the observed chemical changes rather than differences in the adsorption structure of molecularly bound species on the two surfaces.

It is interesting to note that the observed chemistry on the W(100)-(5×1)-C surface is strikingly similar to that observed on oxygen-pretreated Ag(110).[5] Surface stable CH_2CN has been identified in the Ag(110)-O surface which undergoes competing rehydrogenation to regenerate CH_3CN at 500 K and further dehydrogenation. The parent CH_3CN desorption spectra are also similar. It is rather surprising that a surface as active as W(100) is modified by the carbide overlayer such that product distribution and reaction energetics are similar to oxygen treated Ag, which is generally used to effect selective chemistry.

Conclusions

An increase in the stability of CH_3CN with respect to irreversible decomposition has been identified the W(100)-(5×1)-C surface compared to W(100), similar to that reported for HCN.[8] In addition, the -(5×1)-C overlayer induces a significant change in reaction selectivity in comparison to W(100). C–C bond activation and hydrogenation of acetonitrile yield CH_4 as a reaction product on clean W(100), whereas reversible C–H bond activation to regenerate the nitrile predominates on the -(5×1)-C surface. These reactions are significantly different than previously reported for group VIII (groups 8–10)[24] transition-metal surfaces where simple reversible molecular adsorption predominates. There is, however, a striking resemblance between the chemistry on the -(5×1)-C surface and oxygen-pretreated Ag(110).[5]

Spectroscopic studies, namely near edge X-ray absorption fine structure measurements[16] and high-resolution electron energy loss spectroscopy,[17] are planned as a means of characterizing the orientation of the C–N bond vector and identifying the onset of C–H bond activation in the nitrile. These proposed studies may help determine if there is a correlation between the observed surface reactivity and adsorption structure.

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Registry No. W(100), 7440-33-7; W(100)-(5×1)-C, 12070-12-1; CH_3CN, 75-05-8.

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(24) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(25) Note added in proof: Recent vibrational studies evidence N–H bond formation at 400 K.[26] Nitrogen–hydrogen bond scission and accompanying C–H bond formation and proposed to result in the 450 and 550 K CH_3CN peaks.

(26) Serafin, J. G.; Friend, C. M., to be published.

STATISTICAL MECHANICS AND THERMODYNAMICS

On the Mc Activity Coefficient Function Describing Solute and Solvent Equilibria: Methanesulfonic Acid Aqueous Solutions

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Degrees of dissociation of aqueous methanesulfonic acid in the range 0.1–15 M have been determined by Raman spectroscopy, and a thermodynamic dissociation constant $K_{HA} = 35 \pm 10$ mol/L has been estimated. Ionization ratios of some nitroanilines have been also measured by UV. Raman and UV data have been used for determining the Mc activity coefficient function. It has been shown that the Mc function is the best available tool for describing the variation of activity coefficients of univalent acids dissociating in concentrated aqueous acid solutions and determining K_{BH^+} constants for equilibria of indicators.

Introduction

The development of new areas of chemistry in acids and superacids for carrying out equilibria and reactions requires a suitable estimate of "acidity" of concentrated acid solutions. To overcome the failing of the pH scale in nonideal aqueous media, the Hammett approach has been a widely employed method.[1-4] The protonating ability of a given acid solution is measured by com-

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