knowledge of the nature of supported metal oxide catalysts, it cannot yet be concluded whether or not this complex condition of the vanadium catalyst is related to the layered structure. However, we can indicate that the chemical affinity to crystal faces and/or the crystallographic fitness may influence surface condition, as mentioned below.

The coverage behavior of vanadium oxide was related to the electronegativity of cations in its oxides, and some relationship with the surface acid-base properties might also be indicated.⁹ Because the acidic oxide (i.e., V_2O_5) was effectively supported on the basic support, such differences in the acid-base properties could be the cause of the high coverage efficiency of vanadium oxide. In other words, the vanadium oxide could be supported due to the different chemical property of the support. Therefore, vanadium oxide may be supported on alumina with the strongest interaction with the support. In this condition, it may not be easy to form the layer structure of vanadium oxide. On the other hand, when there is little interaction with the support as on SiO_2 , vanadium oxide behaves as if it were unsupported. After all, high exposure of the active (010) face on ZrO_2 and TiO_2 could be understood as resulting from the medium degree of interaction with the support.

The high exposure of active V=O sites on TiO_2 (anatase) was explained on the basis of the crystallographic fitness between anatase and V_2O_5 , as was indicated by Courtine et al.¹⁶ This explanation is significant in the case of anatase. Such a crystallographic fitness could be observed on ZrO_2 and TiO_2 (rutile), since vanadium oxide on these supports exposed active sites similarly on the anatase. On these oxides, however, some alterations of crystal dimensions in the boundary may stimulate the fitness as was indicated for V_2O_5 on TiO₂ (rutile).^{3a}

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Multicomponent Cluster Ions. 2. Comparative Stabilities of Cationic and Anionic Hydrogen-Bonded Networks. Mixed Clusters of Water and Hydrogen Cyanide

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The thermochemistry of cluster ions containing nH_2O and mHCN molecules, for clusters up to rank r = n + m = 5, was obtained from equilibrium measurements. The clustering of H_2O about H_3O^+ and OH^- and the clustering of HCN about HCNH⁺ show distinct shell filling effects, but the clustering of H₂O and HCN about CN⁻ does not. Hydration by one water molecule eliminates the difference of 5 kcal/mol between the proton affinities of HCN and H_2O . Hydration also decreases the difference between the intrinsic deprotonation energies, i.e., ΔH°_{acid} , of H₂O and HCN from 37.7 to 19.8 kcal/mol in the 4-fold hydrated species. In protonated clusters of a given rank r, exchange of H₂O by HCN does not significantly affect the total stability of the cluster. This is in contrast to H_2O/CH_3OH and H_2O/CH_3CN protonated clusters and H_2O/HCN anionic clusters, where increasing nonaqueous content is stabilizing. In the latter, the most stable clusters of any size are the neat CN^{-} nHCN clusters.

Introduction

The properties of clusters are of interest in relation to the transition from gas-phase to condensed-phase behavior, and also in relation to nucleation leading to condensation and aerosol formation in ionized planetary atmospheres. Atmospheres include a mixture of gases, and therefore the properties of multicomponent clusters are important. Water and hydrogen cyanide are common in planetary and interstellar environments and are likely to be contained in cluster ions in such environments. Therefore, we extended our studies on multicomponent clusters to the H₂O/HCN system.

The preceding study in this series dealt with anionic and cationic clusters containing water and methanol.¹ In that study we compared for the first time the stabilities in anionic vs cationic clusters with increasing cluster rank r (r = n + m, where the cluster includes nH_2O and mHCN molecules). The observation was that the bonding energies with cluster growth showed a similar pattern both in the anionic and cationic systems.

In that system, however, an infinite network of strong OH···O hydrogen bonds was possible in both the anionic and cationic clusters. In contrast, in other mixed cluster systems such as $H_2O/(CH_3)_2O^2$ and H_2O/CH_3CN ,³ blocking by methyl groups prohibits clusters of certain composition. The HCN molecule is intermediate in that it contains only a carbon-bonded hydrogen,

Experimental Section

The measurements were done by using the NBS pulsed highpressure mass spectrometer⁴ and procedures as described in preceding papers.^{1,3}

For cationic clusters, the carrier gas was Ar or CH₄ containing 0.1-2.4% H₂O and 0.2-0.7% HCN. The formation of (HCN)₂H⁺ was studied in 1.8% HCN in CH₄, as well as in an $H_2O/$ HCN/CH₄ mixture. The formation of (HCN)₃H⁺ was studied in pure HCN. The formation of $(H_2O)_nH^+$ was studied in 6.4% H_2O in CH_4 . In order to avoid mass coincidence problems, D_2O and DCN had to be used in some experiments. Moreover, clusters involving C₂H₅⁺ from methane also caused mass coincidence problems, and therefore in some experiments Ar was used as the carrier gas.

For anionic clusters, CH₄ was the carrier gas. Trace amounts of CH₃ONO were added for electron capture, yielding CH₃O⁻,

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but it is strongly acidic and therefore relatively strongly hydrogen-bonding. It will be of interest to examine therefore the development of cluster stabilities with cluster composition in this system.

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Figure 1. van't Hoff plots for clustering equilibria of protonated clusters. Notation is the same as in Table I, but H^+ is not shown.

TABLE I: Thermochemistry^{*a*} of Protonated Clusters of $H_2O(W)$ and HCN (C)



 ${}^{a}-\Delta H^{\circ}$ (kcal/mol) is given as the top number and $-\Delta S^{\circ}$ (cal/(mol K)) as the bottom number above each arrow. Values for the formation of C₃H⁺, C₄H⁺, and C₅H⁺ are from ref 11; for W_nH⁺ from refer 8. For C₂WH⁺ \rightarrow C₃WH⁺, ΔH° is calculated from ΔG° (298) = -8.4 kcal/mol; ΔS° estimated from similar reactions. Number under each formula is ΔH° for dissociation to H₃O⁺ and neutrals.

which deprotonates HCN to yield CN⁻. The mixtures contained 0.1-2% H₂O and HCN except for CN⁻nH₂O, n = 2-4, where up to 50% H₂O was used. Some measurements were done with D₂O. In both the anionic and cationic clusters, replacing H₂O by D₂O did not change the thermochemistry measurably in any given clustering step.

The total source pressures ranged from 0.8 to 2.4 Torr. As usual, checks were made to ensure that the equilibrium constant was independent of pressure and mixture composition. In general, the equilibria were run under conditions where the concentration of the higher cluster is smaller than that of the lower cluster. Also, the concentrations of the reactants were kept as low as possible, and this allowed measuring each reaction at as low a temperature as possible. These measures minimize the error associated with



Figure 2. van't Hoff plots for clustering equilibria of protonated clusters. Notation is the same as in Table I, but H^+ is not shown.



Figure 3. van't Hoff plots for ligand-exchange equilibria of protonated clusters. Notation is the same as in Table I, but H^+ is not shown.



Figure 4. van't Hoff plots for clustering equilibria of anionic clusters. Notation is the same as in Table II.

cluster decomposition outside the ion source.

Results

van't Hoff plots for clustering and ligand-exchange equilibria are given in Figures 1-5. The results are summarized in Tables I and II.

For the values obtained from van't Hoff plots, the usual error is $\pm 1 \text{ kcal/mol}$ for ΔH° and $\pm 2 \text{ cal/(mol K)}$ for ΔS° . In several reactions at low temperature, ΔG° was measured at a single temperature, and ΔH° was calculated from $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ by using estimated values for ΔS° . This was done mostly for equilibria where the available temperature range is limited by the condensation of water in the ion source at about -40 °C. It should be noted that for clustering equilibria of large clusters of simple components such as H₂O and HCN, ΔS° is generally in the range 18-26 cal/(mol K), and for ligand exchange, between -4 and 4



Figure 5. van't Hoff plots for ligand-exchange equilibria of anionic clusters. Notation is the same as in Table II.

TABLE II: Thermochemistry^a of Deprotonated Clusters



^a $-\Delta H^{\circ}$ (kcal/mol) is given as top number and $-\Delta S^{\circ}$ (cal/(mol K)) as bottom number above each arrow. Notation: $C_n W_m^- = ((H_2 O)_n^- (H C N)_m - H)^-$. Values for C_n^- are from ref 13; for W_n^- from ref 8. Values for ΔS° in parentheses were estimated from similar reactions, and those for ΔH° were calculated from ΔG° as follows (reaction, ΔG° and those for ΔH were calculated from ΔG^{-} as to how (acation, ΔG^{-} (kcal/mol), T (K)): $CW_{3}^{-} \rightarrow C_{2}W_{2}^{-}$, -4.6 (262); $C_{2}W_{3}^{-} \rightarrow C_{3}W_{2}^{-}$, -3.4 (262); $C_{3}W^{-} \rightarrow C_{4}^{-}$, -3.2 (262); $CW_{3}^{-} \rightarrow CW_{4}^{-}$, -4.6 (262); $CW_{3}^{-} \rightarrow C_{2}W_{3}^{-}$, -7.9 (262); $C_{2}W_{2}^{-} \rightarrow C_{3}W_{2}^{-}$, -7.4 (262); $C_{3}W^{-} \rightarrow$ $C_{3}W_{2}^{-}$, -3.7 (262); $C_{3}W_{2}^{-} \rightarrow C_{4}W^{-}$, -3.8 (262); $C_{3}W^{-} \rightarrow C_{4}W^{-}$, -7.1 (262); $C_{4}^{-} \rightarrow C_{4}W^{-}$, -4.2 (262); $CW_{4}^{-} \rightarrow C_{2}W_{3}^{-}$, -4.1 (262).

cal/(mol K).⁵ Estimating ΔS° for the two processes as 20 ± 4 and 0 ± 4 cal/(mol K), respectively, at 300 K introduces an uncertainty of ± 1.2 kcal/mol to the calculated value of ΔH° . This is similar to the error of experimental temperature studies. Therefore, for low temperatures, single temperature measurements are comparable in value to the more demanding temperature studies.

From the measured thermochemistry, we calculate the total stabilization of each cluster, i.e., the enthalpy of dissociation to the highest energy component, H_3O^+ or OH^- . The energy for each cluster of rank r (where r = n + m) is calculated from the



Figure 6. Enthalpy sequences, $\Delta H^{\circ}_{n-1,n}$ vs *n* for cationic clusters.



Figure 7. Enthalpy sequences, $\Delta H^{\circ}_{n-1,n}$ vs *n* for anionic clusters.

energies of the clusters of rank r - 1 by using each available path as described previously.¹ The error assigned to each path is the cumulative expected error, i.e., for a path of n steps, each with an error of ± 1 kcal/mol, $n^{1/2}$ kcal/mol. The final value assigned to each cluster is the weighted average of the values derived from all available paths.

The ΔH° values for proton transfer from H₂O to CN⁻ and from H_3O^+ to HCN are quoted from acidity⁶ and proton affinity⁷ tables. The results for the pure water clusters, which are quoted from our previous work,⁸ are in good agreement with the most recent values from Kebarle's laboratory.^{9,10} For $(HCN)_{\eta}H^+$ the present measurements repeat a preceding study on another mass spectrometer.¹¹ For $(HCN)_2H^+ + HCN$, the present result agrees well with the previous value. For $HCNH^+ + HCN$, the present ΔH° and ΔS° results are somewhat lower than the previous results of 30.0 kcal/mol and 32 cal/(mol K). However, the present values are supported by the consistency of the thermochemical cycles in Table I. Thus, in the notation of Table I, ΔH° for CH⁺ \rightarrow C_2H^+ is 26.1 kcal/mol from the direct measurement, 26.8 from $CH^+ \rightarrow CWH^+ \rightarrow C_2H^+$ and 25.8 from $CH^+ \rightarrow WH^+ \rightarrow W_2H^+ \rightarrow CWH^+ \rightarrow C_2H^+$. This consistency also helps to verify the result used here for the water dimer. In general, thermochemical cycles in Figures 6 and 7 are consistent within 2.5 kcal/mol for ΔH° and 4 cal/(mol K) for S° , which is consistent with the error of ± 1 kcal/mol and ± 2 cal/(mol K) assigned to the individual steps.

Discussion

1. Stepwise Buildup of Clusters and Solvent Shell Effects. The enthalpy sequences for the consecutive addition of neutrals to the cationic clusters are shown in Figure 6 and for anionic

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clusters in Figure 7. The buildup of water clusters shows well-defined shell effects after the filling of the first solvent shell in H_3O^+ · $3H_2O$ and OH^- · $3H_2O$, as was discussed before,⁸ and as is more evident from continuing the enthalpy sequences to higher clusters, up to n = 8. The clustering of HCNH⁺ by HCN also shows a possible shell effect after HCNH⁺·HCN. This is indicated by the relatively large drop in attachment energy after the first ligand as expressed by $\Delta H^o_{1,2}/\Delta H^o_{0,1} = 0.55$, which is larger than the usual value of 0.7–0.8. This is consistent with the filling of the first solvent shell about the proton in HCN·H⁺·NCH, as suggested before.¹¹ The sequence also shows a somewhat steep drop after HCNH⁺·3HCN, where the sequence fails to show at this step the usual asymptotic curvature. This effect, although small, is consistent with the filling of a second solvent shell in the linear structure HCN·HCN·H⁺·NCH·NCH.

The enthalpy sequence for HCNH⁺ $\cdot n$ H₂O decreases smoothly from n = 1 to 3, indicating an absence of distinct shell effect. This series is analogous to CH₃CNH⁺ $\cdot n$ H₂O, where ab initio studies show that the proton shifts to H₂O after the second H₂O molecule is added, to form a cluster about the multiply hydrogen-bonding H₃O⁺ as the ionic center.³ Such a shift is even more favored from HCNH⁺ to H₂O, since the proton affinity difference between HCN and H₂O is only 4.9 kcal/mol. Therefore, in all of the present clusters with r > 2, the ionic center is probably H₃O⁺. Moreover, a shift may occur already in HCNH⁺·H₂O, since the proton affinity difference may be overcome by the stronger iondipole forces in H₃O⁺·NCH where the more polar component is the neutral entity. This point merits a theoretical study.

The enthalpy sequences in the anionic clusters parallel those of the cationic clusters. Here also the water clusters $OH^{-}nH_2O$ show shell filling after n = 3, because of the three electron lone pairs in $OH^{-,8}$ In comparison, $CN^{-}nHCN$ does not show a distinct structure. However, the lack of the usual asymptotic decrease through n = 2 suggests a small shell effect at this step, after the first shell is filled about the central ion in the linear cluster NCH·CN⁻·HCN. While the linear structure is favored here, it is only slightly more stable than branched structures, and a shell of up to four HCN molecules may build up about $CN^{-,13}$

Finally, $CN^{-}nH_2O$ is the most weakly solvated cluster. The hydration energies after the first step approach too closely the limiting value, $\Delta H^{\circ}_{vap}(H_2O) = 10.5 \text{ kcal/mol}$, to allow a noticeable shell effect.⁸

As we noted, HCN·H⁺·NCH completes the first solvent shell, and further clustering must be through less efficient CH···N type bonds. While the blocking here is less drastic than in CH₃CNH⁺ NCCH₃, it is sufficient to destabilize the neat HCN clusters after the dimer. Therefore, the cationic neat HCN clusters are not competitive in stability with H₂O-clusters (Table I). As a result, HCN is a poorer solvent for the proton in large clusters than H₂O and other hydrogen-bonding solvents such as CH₃OH and NH₃.

In contrast to the protonated neat HCN clusters, in CN-*n*HCN no significant drop in bonding energies, due to shell effects, is noted at any step. The neat anionic HCN clusters therefore remain more stable than H_2O -containing neat or mixed clusters at any rank r = n + m clustering. Therefore, HCN is a more efficient solvent for an anionic "proton hole" than H_2O or CH₃OH, and it may be one of the most efficient such solvents among neat organic compounds.

The absence of noticeable shell effects in the clustering of H_2O and HCN about CN⁻ further demonstrates that CN⁻ behaves as a spherical ion similar to Cl⁻ or Br⁻; i.e., the bonding of ligands to C or N in the smaller clusters, and the bonding to CN⁻ at the CN bond vs bonding to the first ligands in the larger clusters, are of comparable energies.¹³ Therefore, the rank r = 2-5 clusters observed under our conditions may constitute an equilibrium mixture of isomeric structures. This may be quite common for large cluster ions in general.⁸

2. Effects of Hydration on Relative Acidities and Basicities. Protons attached to weaker bases are shared more efficiently with the solvent, and stabilized more by solvation, than protons attached to strong bases. The result is that solvation tends to compress the gas-phase differences in acidities and basicities. In the present case, this is observed in the first solvation step of H_3O^+ vs HCNH⁺, which eliminates the difference between the basicities of the corresponding neutral molecules. However, further hydration steps have no significant effects. The stabilities of $H_3O^+ \cdot nH_2O$ and HCNH⁺ $\cdot nH_2O$ remain similar; i.e., the proton affinities of the *n*-fold hydrated HCN and H_2O are similar (Table I).

In the case of the anions, hydration has a larger effect, which increases with increasing hydration. The acidity difference of 37.7 kcal/mol is reduced to 25.5 kcal/mol by the first H_2O molecule and is further reduced to 19.5 kcal/mol by four H_2O molecules. Nevertheless, up to the largest clusters observed, hydration is not sufficient to reverse the large initial difference in acidities.

3. Effects of the Substitution of H₂O Molecules by HCN. In mixed clusters of H₂O with CH₃CN and CH₃OH, the nonaqueous component has a substantially larger basicity, i.e., charge-stabilizing capacity. As a result, the gradual substitution of H₂O by CH_3CN or CH_3OH molecules in a cluster of a given rank r is always stabilizing (except for blocked clusters). The trend is different in the present H_2O/HCN protonated clusters. Here, the proton affinity of HCN is only slightly larger than that of H_2O . Except for the first hydration step, the greater polarity of HCN seems to be compensated by the stronger hydrogen-bonding capacity of H_2O to form $OH \cdots O$ type hydrogen-bonded networks. Therefore, the mixed clusters show no preference for H₂O or HCN, and clusters of a given rank have similar stabilities regardless of composition. This would probably continue beyond the rank 4 clusters observed here, since all (except $H_3O^+ \cdot nHCN$ clusters) can be derived from preceding clusters by adding an H₂O molecule. These additional hydration energies usually level off to a constant value of about ΔH° (condensation) (H₂O) = 10.5 kcal/mol for r = 4 to 8^{14} and may remain constant also for higher steps. Even if the attachment energies decrease further, the attachment energies of a further H₂O molecule to clusters of a given rank r and of different compositions are not expected to be significantly different, especially for clusters that contain several H₂O molecules. This is because all such larger clusters will have a highly diffuse charge, and they will all have attachment sites for multiple neutral-like OH···O hydrogen bonds. Since the stabilities of the presently observed smaller clusters of a given rank are independent of composition, this trend is therefore expected to carry on for larger clusters. Exceptions are blocked clusters such as H_3O^+ ·3HCN, where adding further HCN molecules should be unfavorable, making clusters containing only one H₂O molecule less stable.

In contrast to the cationic clusters, the much greater acidity of HCN vs H_2O carries through in the anionic clusters. At any size, HCN is a sufficiently stronger hydrogen donor, and exchanging H_2O with HCN is always stabilizing. As a result, the stability of the cluster always increases with HCN content. The most stable anionic cluster of any rank is the neat HCN cluster.

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