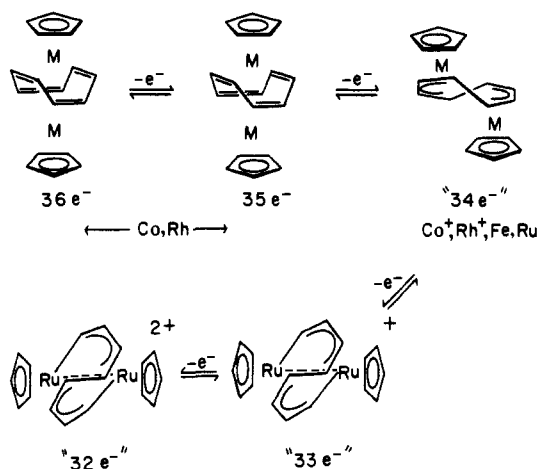


Scheme II



the C_8 ring. Scheme II summarizes the known structural preferences.

The thermodynamically favored structures are given in each case with the structure of the $35 e^-$ species being the only one in

serious question. The question mark for the $35 e^-$ species relates to uncertainty of whether the observation of the tub form of $[Cp_2Rh_2(\mu-C_8H_8)]^+$ (see preceding paper in this issue) has its origin in the kinetic or thermodynamic preference of the $35 e^-$ species.

Note that the formal electron count in this scheme is derived employing a constant number of valence electrons for both the C_8H_8 ligand ($8 e^-$) and the CpM moieties ($14 e^-$ for $CpRh$, $13 e^-$ for $CpRu$). This emphasizes the electron-deficient nature of the metals in the $34 e^-$ and $32 e^-$ species. However, the metals form new bonds after each two-electron transfer, thereby retaining the $18 e^-$ structure in each even-electron species. Thus, when the " $34 e^-$ " species is formed, the bridging C-C bond of the cyclooctatetraene ligand donates an extra electron to each metal, thereby achieving coordinative saturation. Similarly, M-M bond formation provides another valence electron to each metal in the " $32 e^-$ " species. In simple terms, then, the stability of the $18 e^-$ configuration for each metal provides a rationalization of the even-electron structures of the entire series.

Acknowledgment. W.E.G. gratefully acknowledges the support of this research by the National Science Foundation (CHE86-03728). A.S. and W.v.P. thank the Swiss National Science Foundation for Grants 20-5406.87 and 2000-4.933.

Experimental Study of HCN^+ and HNC^+ Ion Chemistry

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Abstract: We report the results of a room temperature selected ion flow tube study of reactions of HCN^+ and HNC^+ . Electron impact on HNC was found to produce a mixture of HCN^+ and HNC^+ isomers. HCN^+ was found to be isomerized efficiently to HNC^+ by reaction with CO or with CO_2 , and isomerization is expected to occur for any other species M having a proton affinity $PA(CN \text{ at } C) < PA(M) < PA(CN \text{ at } N)$. The isomerization process is interpreted in terms of a "forth and back" proton transfer mechanism. A monitor gas technique was used to distinguish between the isomers. With CF_4 , HCN^+ was reactive ($k = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) and HNC^+ unreactive. With SF_6 both isomers react at the collision rate but HCN^+ yields only SF_5^+ as the product ion whereas HNC^+ yields only $HNCF^+$. Thermodynamic data established in this work include $\Delta H_f(HNC^+) \leq 1373 \text{ kJ mol}^{-1}$, and hence $PA(CN \text{ at } N) \geq 595 \text{ kJ mol}^{-1}$.

Introduction

The present investigation is a continuation of the study of isomeric ion chemistry involving small ions of astrophysical interest carried out recently in this laboratory. Previous studies, utilizing the selected ion flow tube (SIFT) technique, have involved CH_3CNH^+/CH_3NCH^+ ,¹ HCO^+/HOC^+ ,² and CNC^+/CCN^+ ³ isomers. Other groups that have examined isomeric structures in flow tubes include Smith and Adams⁴ and Bohme et al.⁵ The reactions are measured in a flow tube with mass spectrometric detection. The identical mass isomeric ions are distinguished on the basis of their different reactivities with selected neutrals. This variation of the so-called "monitor ion" technique involves the addition of a neutral monitor reactant gas prior to mass analysis. In an ideal situation, the reaction of the monitor gas is exothermic and fast with the most energetic isomer and endothermic and does not occur with the more stable isomer. However, different isomeric forms have been distinguished when both isomers react, but at very different rates. The monitor ion technique was first used

in Flowing Afterglows to distinguish electronically excited metastable ions from ground-state ions in order to study the reactivities of electronically excited ions.⁶ Recently the monitor ion technique has been utilized to distinguish between ions in different vibrational states in order to measure collisional⁷ and radiative⁸ ion vibrational relaxation.

In the present study two suitable monitors were found that enable HCN^+ and HNC^+ to be readily distinguished in a flow

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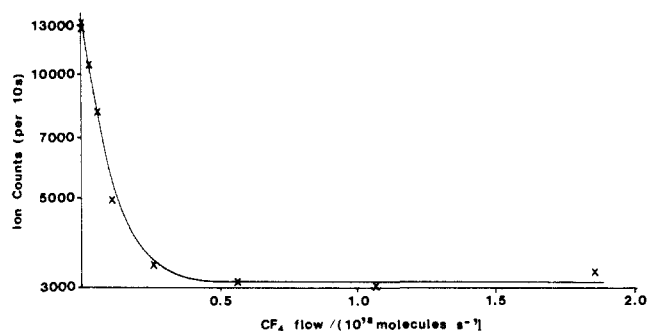


Figure 1. Semilogarithmic plot for the ion count rate at $m/z = 27$ against CF_4 flow. The $\text{HCN}^+/\text{HNC}^+$ mixture was generated by electron impact on HCN. The points are experimental and the curve was fitted to the double exponential decay by least squares.

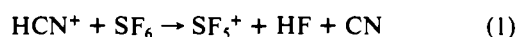
tube. With CF_4 as the monitor gas, HCN^+ was reactive and HNC^+ unreactive. With SF_6 as the monitor gas both isomers reacted at similar rates but HCN^+ yielded only SF_5^+ as the product ion whereas HNC^+ yielded only HNCF^+ as the product ion.

Experimental Section

All measurements were carried out at room temperature, 300 ± 5 K, in a SIFT apparatus described elsewhere.⁹ The ions HCN^+ and HNC^+ were produced by subjecting HCN to 30 eV electron impact in the ion source and injecting the resultant isomeric mixture at $m/z = 27$ into the flow tube. SF_6 and CF_4 were obtained commercially at better than 99.5% purity and were subjected to further freeze-pump-thaw cycles. HCN was prepared from concentrated H_3PO_4 on KCN followed by trap-to-trap distillation after drying.

Results

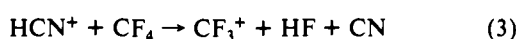
The rate coefficients and products for the reactions of $\text{HCN}^+/\text{HNC}^+$ with the monitor gases SF_6 and CF_4 are as follows:



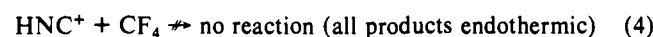
$$-\Delta H_1 = 12 \pm 10 \text{ kJ mol}^{-1}; k_1 = 1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$



$$-\Delta H_2 \sim 132 \text{ kJ mol}^{-1}; k_2 = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$



$$-\Delta H_3 = -9 \pm 20 \text{ kJ mol}^{-1}; k_3 = 1.15 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$



The identification of the isomers HCN^+ and HNC^+ was made in the following way. With HCN in the ion source, all ions at $m/z = 27$ were selected by the upstream quadrupole mass spectrometer and injected into the flow tube. When CF_4 was used as the neutral reactant, the ion signal at $m/z = 27$, I_{27} , was recorded for each flow rate of CF_4 and a semilogarithmic plot of I_{27} versus CF_4 flow obtained in the usual way (see Figure 1). Two components were apparent in the I_{27} decay; one component was indicative of an ion at $m/z = 27$ that reacted rapidly with CF_4 and the other component was nonreactive. The reactive component was present in the larger amount and was identified as HCN^+ , in keeping with the use of HCN as the source gas and on the basis of the enthalpy data available on the $\text{HCN}^+/\text{HNC}^+$ system. Ab initio studies on the two isomers have identified $\Delta H_f(\text{HCN}^+)$ to be greater than $\Delta H_f(\text{HNC}^+)$ by $\sim 90 \text{ kJ mol}^{-1}$,¹⁰⁻¹² and the higher energy species is more reactive. Previous experiments with a different technique have also shown that

HCN^+ was the isomer present in greater amount when HCN was subjected to electron impact.¹³ The possibility of vibrational or metastable excitation of HCN^+ being responsible for the reactive component and ground-state HCN^+ for the nonreactive component can be discounted as such a view is inconsistent with the known thermochemistry of HCN^+ . Further, the addition of N_2 to the isomeric mixture did not alter the ratio of the two components, whereas the addition of a similar amount of CO caused the complete conversion of the reactive form into the nonreactive form. Such an observation is consistent with the "forth and back" mechanism of proton transfer discussed later in this paper (which occurs with CO) and is inconsistent with vibrational quenching. In the latter case an effect of similar magnitude would be expected for both N_2 and CO. The identification of the reactive and nonreactive components was confirmed by producing the lower energy isomer only, HNC^+ , in the flow tube by adding either CO or CO_2 at the first inlet port. The ensuing reaction of HCN^+ with CO or CO_2 converted the more reactive HCN^+ isomer in the mixture into HNC^+ via reactions 6 and 10 as discussed later in this work. When SF_6 was used to determine the $\text{HCN}^+/\text{HNC}^+$ ratio in the presence of CO or CO_2 , there was no evidence for subsequent reactions of either SF_5^+ or HNCF^+ with either CO or CO_2 . The ratio of the intercepts of the two parts of the curve in Figure 1 gives the $\text{HCN}^+/\text{HNC}^+$ ratio. The slight exothermicity of reaction 1 and hence the probable occurrence of this reaction was anticipated in view of recent determinations of $\text{AP}(\text{SF}_5^+/\text{SF}_6) = 13.98 \pm 0.03 \text{ eV}$.^{14,15} This value is markedly lower than that currently listed in tables of $\text{AP}(\text{SF}_5^+/\text{SF}_6) = 15.33 \pm 0.03 \text{ eV}$ ¹⁶ and represents a striking example of the large differences that are possible between vertical appearance potentials measured by photon and electron impact and adiabatic potentials of relevance to thermodynamics. See also Note Added in Proof. Thermal energy ion-molecule reactions characteristically behave adiabatically, i.e. they are efficient when exothermic, without Franck-Condon constraints and without barriers on the potential energy surface when electronic transitions are not involved.¹⁵

The exothermicities given above utilize energies taken from the most recent NBS thermochemical compilation,¹⁶ except for the heats of formation of SF_6^+ and CF_3^+ (obtained from adiabatic appearance potentials¹⁴ that are very much lower than previously reported values¹⁶). In the case of reaction 1 the $\pm 10 \text{ kJ mol}^{-1}$ uncertainty is the listed uncertainty in $\Delta H_f(\text{CN})$, which in turn goes back to the uncertainty in $\Delta H_f(\text{HCN})$. However, the uncertainty in each of reactions 1 and 3 may be reduced by not including the uncertainty in $\Delta H_f(\text{HCN})$ in the thermochemical cycle used to evaluate the energy change for these reactions. On the left side of the equation for reaction 1, the ionization potential of HCN is known precisely¹⁷ ($13.60 \pm 0.01 \text{ eV}$), and on the right side the appearance potential of $\text{H}^+ + \text{CN}$ from HCN is known precisely to be $19.00 \pm 0.01 \text{ eV}$,¹⁸ and of course $\Delta H_f(\text{H}^+)$, $\Delta H_f(\text{F})$, and $\Delta H_f(\text{HF})$ are all precisely known so that the exothermicity of reaction 1 so derived is $12 \pm 6 \text{ kJ mol}^{-1}$, where the major factor in the uncertainty is that of the $\text{AP}(\text{SF}_5^+/\text{SF}_6)$. The observation of this fast, and exothermic, reaction supports the lower value of $\text{AP}(\text{SF}_5^+/\text{SF}_6)$ to within the exothermicity of the reaction, viz 12 kJ mol^{-1} or $\sim 0.1 \text{ eV}$.

In the case of reaction 3, the literature values for heats of formation predict an endothermic reaction that is clearly incorrect (since this fast reaction is obviously exothermic). The large error limit of 20 kJ mol^{-1} does permit an exothermic reaction, however, and the observation of reaction 3 allows us to refine the thermochemistry. The $\pm 20 \text{ kJ mol}^{-1}$ includes the $\pm 10 \text{ kJ mol}^{-1}$ associated with CN which can be removed, as discussed above for

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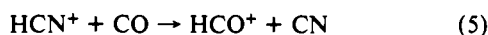
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reaction 1, since with HCN⁺ as reactant and CN as product the uncertainty in the heat of formation of HCN cancels. The remaining 10 kJ mol⁻¹ uncertainty arises from the AP(CF₃⁺/CF₄) = 14.2 ± 0.1 eV obtained from bracketing experiments.^{14,15} In order to satisfy the evident exothermicity of reaction 3, ΔH_f(CF₃⁺) must be less than 347 kJ mol⁻¹, or AP(CF₃⁺/CF₄) ≤ 14.1 eV. Since the lower limit of AP(CF₃⁺/CF₄) is tightly constrained also, by values of IP(CF₃) and D(CF₃-F), we believe that a value for the AP(CF₃⁺/CF₄) = 14.05 ± 0.05 eV (or ΔH_f(CF₃⁺) = 341 ± 5 kJ mol⁻¹) has conservative error limits.

The reaction of HNC⁺ with SF₆ (reaction 2) was not anticipated as the exothermic channel to HNC⁺ was initially overlooked. It was thought that as production of SF₅⁺ was endothermic, the reaction would not go. However, since the products of the HCN⁺ and HNC⁺ reaction with SF₆ are different, it serves as an ideal monitor as measurement of the product ratio (SF₅⁺/HNC⁺) is a direct measure of the isomer ratio (HCN⁺/HNC⁺). In the present experiment, ionization of HCN with a broad electron energy distribution around 30 eV produced an HCN⁺/HNC⁺ ratio of ~3. It has been previously reported that electron impact on HCN produces more than 70% HCN⁺ ions.¹³

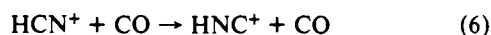
Coincidentally, and probably no more than that, the 3:1 isomer ratio is just the ratio of statistical weights of HCN⁺ (2Π) to HNC⁺ (2Σ). We plan to examine this ratio as a function of the ionizing electron energy and also with photon and charge-transfer ionization. One can also use the present monitor technique to measure the HCN⁺/HNC⁺ ratio from ionization of more complex molecules such as methylamine, dimethylamine and methyl isocyanide.

The present investigation was motivated in part by the observation that reaction 5 was extremely slow. The occurrence



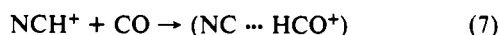
$$-\Delta H_5 = 73 \text{ kJ mol}^{-1}; k_5 \sim 3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

of slow exothermic proton transfer in such simple systems is so rare as to be almost non-existent, which made the observation very puzzling. The solution of this puzzle was the realization that the reaction of HCN⁺ with CO is fast but that the major product of the reaction is not HCO⁺ but HNC⁺. With mass spectrometric detection the production of HNC⁺ appears as a nonreaction, the product of course being the same mass as the reactant ion. Only in the presence of the monitor was the isomerization reaction revealed to occur at about half the Langevin rate of 9.1 × 10⁻¹⁰ cm³ s⁻¹. We propose a two-step proton transfer from HCN⁺ to



$$k_6 = 4.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

CO followed by proton transfer back to CN to produce the more stable HNC⁺ within the complex before separation occurs, as in reactions 7 and 8:

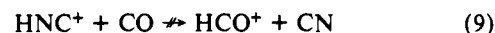


followed by



Reaction 7 is clearly exothermic and approaches 73 kJ mol⁻¹ exothermicity at large NC ⋯ HCO⁺ separations. Reaction 8 is also exothermic in view of the large HNC⁺/HCO⁺ ratio observed in the experiment (~2 × 10²), but as the heat of formation of HNC⁺ is not well established, the exothermicity of reaction 8 is somewhat uncertain. During step 8 a facile rotation of the CN in the complex is required and this is facilitated by the large dipole moment of CN (1.45 D) which favors the CN ⋯ HCO⁺ orientation. We note that the mechanism of proton transfer within the complex has been suggested in several studies of H,D exchange.¹⁹⁻²¹

If the reaction CN + HCO⁺ → HNC⁺ + CO is to be exothermic, as we believe from the efficiency of reaction 6, then it is necessary that ΔH_f(HNC⁺) < 1373 kJ mol⁻¹. This heat of formation is inconsistent with the value of 1407 kJ mol⁻¹ given in the NBS tables,¹⁶ deduced from high-energy charge-exchange breakdown curves²² and theoretical values for ΔH_f(HNC).²³ It is, however, consistent with theoretical calculations of ΔH_f(HNC⁺) = 1322 kJ mol⁻¹¹¹ and 1360 kJ mol⁻¹¹⁰ which we believe are more reliable than the very indirect experimental approach. It is also consistent with our observation that reaction 9 was not observed in our SIFT (k₉ < 1 × 10⁻¹¹ cm³ s⁻¹) and was therefore almost certainly endothermic. Because HCN⁺ reacts with CO, whereas



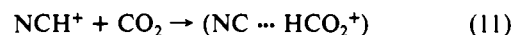
HNC⁺ does not, we thus have a way of converting a mixture of HCN⁺ and HNC⁺ entirely into HNC⁺ in the flow tube.

An interesting test of the mechanism presented here would be to carry out the reaction between HCN⁺ and CO, reaction 6, as a function of KE in a drift tube. Presumably as the relative KE is increased the (NC ⋯ HCO⁺) lifetime would decrease, decreasing the time available for NC to rotate and then abstract a proton from HCO⁺. We would predict therefore that the fraction of collisions leading to HCO⁺ production should increase sharply with KE and we plan to test this hypothesis when a drift tube under construction is added to the present SIFT.

The reaction of HCN⁺ with CO₂ also exhibited very similar behavior to reaction 6 in that isomerization was the major product channel with a rate coefficient k₁₀ = 5.0 × 10⁻¹⁰ cm³ s⁻¹.



Again the mechanism involves exothermic proton transfer to CO₂



$$-\Delta H_{11} \leq 20 \text{ kJ mol}^{-1}$$

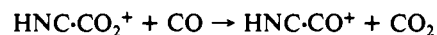
followed by exothermic proton transfer back to the N atom of NC.



This process of isomerization would be expected to occur for any species M for which both proton transfer processes are exothermic, i.e. for any M for which PA(CN at C) < PA(M) < PA(CN at N) or 521 kJ mol⁻¹ < PA(M) < ~595 kJ mol⁻¹.

A minor product channel of the reaction between HCN⁺ and CO₂ is charge transfer which accounts for ~0.3% of the total reaction. The size of this product channel is in accord with the 16 kJ mol⁻¹ endothermicity of this charge-transfer reaction, by k = k_Le^{-ΔE/kT} where k_L is the Langevin rate coefficient.

The reaction between HNC⁺ and CO₂ is also very slow (k = 1 × 10⁻¹² cm³ s⁻¹) at a tube pressure of 0.30 Torr with helium as the buffer gas. The major ion product observed in the experiment was the cluster ion HNC·CO⁺, which we assume was produced by the secondary ligand switching reaction



(CO was present in the reaction tube to isomerize HCN⁺ to HNC⁺.) The product HNC·CO₂⁺ was also observed for this reaction.

We have recently carried out a study of some ion-molecule reactions of dicyanogen²⁴ and in the course of that work we observed that an ion of mass 27 was formed as a product in the reaction of C₂N₂⁺ and HCN (reaction 13). The product HCN⁺ at mass 27 is 23 kJ mol⁻¹ endothermic to charge transfer from

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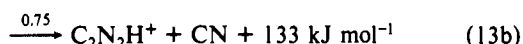
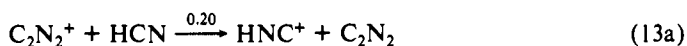
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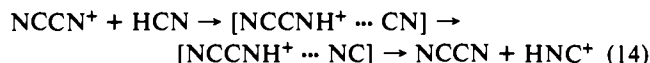
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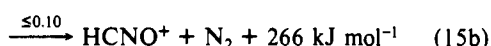
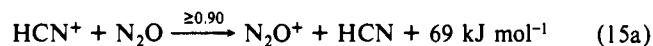
C_2N_2^+ and should therefore not occur. This apparent difficulty was removed upon our identification of the ion at $m/z = 27$ as HNC^+ , which is exothermic to charge transfer by $-\Delta H_{13a} > 50 \text{ kJ mol}^{-1}$. The overall rate coefficient k_{13} is $2.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in a helium buffer gas at 0.3 Torr. The mechanism for reaction 13a is assumed to be



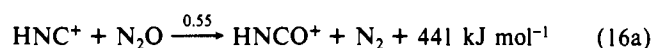
where exothermic hydrogen atom abstraction from HCN is followed by proton transfer back to NC. As in reaction 8, the required rotation of CN is presumably facilitated by the anisotropy of the potential resulting from the large CN dipole moment (1.45 D). In reaction 14 the second proton transfer from NCCNH^+ to NC to produce HNC^+ is endothermic for NCCNH^+ in its ground vibrational level. The first hydrogen atom transfer is exothermic, however, by up to 133 kJ mol^{-1} and sufficient excitation must therefore be retained in the short-lived complex to carry out the $\geq 81 \text{ kJ mol}^{-1}$ endothermic proton transfer to N of NC. Since three-body association is also observed, one can estimate the lifetime of the transient complex from the three-body association rate coefficient ($k_{13c} = 0.05 \times 2.7 \times 10^{-9} / n_{\text{He}} = 1.4 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}$, n_{He} = number density of helium atoms in molecules cm^{-3}). As $k_{\text{assoc}} \sim k_1 k_2 \tau$ (k_1, k_2 are the respective collision rates of C_2N_2^+ on HCN and $\text{C}_2\text{N}_2\text{HCN}^+$ on He) then $\tau \sim 10^{-8} \text{ s}$. This implies a relatively long-lived complex reflecting an appreciable potential well for the complex and a large number of degrees of freedom. A complex of this lifetime implies a substantial randomization of energy in the various modes of the complex, which in turn implies that a large fraction of the energy distribution is effective in transferring the proton from NCCNH^+ to NC. If this transfer were exothermic for ground-state reactants it would surely dominate the breakup of the complex and the major product of reaction 13 would be HNC^+ .

Again an informative experiment would be to measure reaction 13 as a function of relative KE. We would expect the NCCNH^+ channel to become more dominant as the KE increases and the complex lifetime decreases.

Both HCN^+ and HNC^+ react at the collision rate with N_2O but yield different products. Because HCN^+ and HNC^+ were



$$k_{15} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

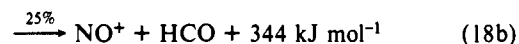
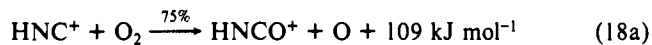


$$k_{16} = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

both present in the flow tube when the reactions of HCN^+ were being studied, and HNCO^+ is the major product of the $\text{HNC}^+ + \text{N}_2\text{O}$ reaction, it was not possible to entirely eliminate HCNO^+ as a product of reaction 15. The major product channel for reaction of HCN^+ with N_2O is charge transfer, whereas charge transfer is endothermic from HNC^+ in reaction 16. An unexpected product channel in the reaction of HNC^+ with N_2O was the production of NO^+ . This channel must also produce HNCN as the accompanying neutral, as the formation of the alternative neutral products $\text{HCN} + \text{N}$ or $\text{NH} + \text{CN}$ is endothermic. The radical HNCN is not well-known although its parent neutral, NH_2CN (cyanamide), is well-known. For the NO^+ channel to be exothermic, the value of $\Delta H_f(\text{HNCN}) \leq 471 \text{ kJ mol}^{-1}$, which

implies an NH bond energy of $\leq 555 \text{ kJ mol}^{-1}$ for NH_2CN . Such a value is reasonable when compared with N-H bond energies in similar compounds (e.g. HNCO and NCO).

In a similar fashion, the reactions of HCN^+ and HNC^+ with O_2 are observed to have comparable rate coefficients but yield different products. Charge transfer is the only product channel attributed to HCN^+ , but it is not observed for HNC^+ .

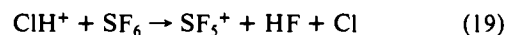


The absence of the charge-transfer channel (18c), in a system where the reactive collisions account for only half of those expected from the calculated collision rate coefficient ($k_{18} = 3.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; $k_c = 7.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$), indicates that this charge-transfer channel is endothermic. Thus $\text{IP}(\text{HNC}) < 1165 \text{ kJ mol}^{-1}$ (this value being the ionization potential of O_2). This further constrains $\Delta H_f(\text{HNC}^+)$: using $\Delta H_f(\text{HNC}) = 201 \pm 8 \text{ kJ mol}^{-1}$,²³ $\Delta H_f(\text{HNC}^+) \leq 1373 \text{ kJ mol}^{-1}$.

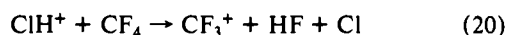
A summary of all the reactions studied in this work is given in Table I.

Discussion

The facile F^- abstractions from SF_6 and CF_4 by HCN^+ to produce SF_5^+ and CF_3^+ are similar to the chemistry of HCl^+ with SF_6 and CF_4 .¹⁴ The reactions 19 and 20 are both fast and have been viewed as F^- abstractions to yield the unstable ClHF which



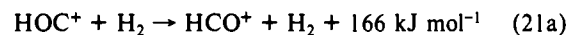
$$k_{19} = 1.25 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$



$$k_{20} = 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

immediately dissociates by the most exothermic pathway (and by the only exothermic reaction possible) to give HF and Cl .¹⁴ In the present case the F^- abstractions are followed by dissociation of CNHF to $\text{CN} + \text{HF}$, again the only exothermic possibilities for reactions 1 and 3. The study of the reactions of HCl^+ with SF_6 and CF_4 formed the basis of the presently accepted heats of formation of SF_5^+ and CF_3^+ and these are supported by the present HCN^+ measurements. Reaction 3 actually gives a new lower estimate for $\Delta H_f(\text{CF}_3^+)$ of $341 \pm 5 \text{ kJ mol}^{-1}$ as the rate coefficient is indicative of an exothermic reaction. Fehsenfeld in an earlier study of similar F^- abstraction reactions²⁵ noted that SF_5^+ was produced together with the neutral fluorides of the ions C^+ , N^+ , O^+ , and CO^+ .

It is interesting to compare the present results using the understanding we have gained from this study, with the results reported earlier in an analogous isomerization study of $\text{HOC}^+/\text{HCO}^+$ ions with H_2 .²



In this study the overall rate coefficient was observed as $4.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which is about $k_L/3$, and the branching ratios as 0.43 for reaction 21a and 0.57 for reaction 21b. Here k_L represents the Langevin rate coefficient for reaction 21. The rate coefficient for the isomerization channel (reaction 21a) is approximately equal to that for the H_3^+ channel (reaction 21b), and their sum is about $1/3$ of k_L . Thus $k_{21a} \sim k_L/6$, $k_{21b} \sim k_L/6$, and $k_{21c} \sim 2k_L/3$. From the magnitudes of the observed proton-transfer rate constants of HOC^+ with H_2 , O_2 , and Kr it can be deduced that $\Delta H_f(\text{HOC}^+) > 991.6, 991.6, \text{ and } 992.8 \text{ kJ mol}^{-1}$, respectively, simply equating

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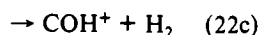
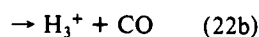
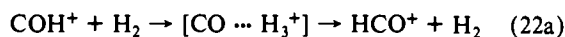
Table I. Rate Coefficients and Branching Ratios for Reactions of HCN⁺, HNC⁺, and Other Cations Measured at Room Temperature in Units of 10⁻⁹ cm³ s⁻¹

reaction	branching ratio	<i>k</i> (this work)	<i>k</i> _{coll} ^a	-Δ <i>H</i> _f ^{b,c} kJ mol ⁻¹
HCN ⁺ + SF ₆ → SF ₅ ⁺ + HF + CN	1.0	1.3	1.2	12 ± 6
HNC ⁺ + SF ₆ → HNC ⁺ + SF ₅	1.0	1.2	1.2	~132
HCN ⁺ + CF ₄ → CF ₃ ⁺ + HF + CN	1.0	1.2	1.0	>0
HNC ⁺ + CF ₄ → no reaction			1.0	
HCN ⁺ + CO → HNC ⁺ + CO	0.99	0.46	0.91	~74
HCN ⁺ + CO → HCO ⁺ + CN	0.01			
HNC ⁺ + CO → no reaction			0.91	73
HCN ⁺ + CO ₂ → HNC ⁺ + CO ₂	≥0.99	0.50	0.98	~74
HCN ⁺ + CO ₂ → CO ₂ ⁺ + HCN	0.003			
HNC ⁺ + CO ₂ → products including HNC-CO ₂ ⁺		0.0012	0.98	-16
C ₂ N ₂ ⁺ + HCN → HNC ⁺ + C ₂ N ₂	0.20	2.7	3.3	52
C ₂ N ₂ ⁺ + HCN → C ₂ N ₂ H ⁺ + CN	0.75			
C ₂ N ₂ ⁺ + HCN → C ₂ N ₂ HNC ⁺	0.05			
HCN ⁺ + N ₂ O → N ₂ O ⁺ + HCN	≥0.90	1.2	1.04	69
HCN ⁺ + N ₂ O → HCNO ⁺ + N ₂	≤0.10			
HNC ⁺ + N ₂ O → HNC ⁺ + N ₂	0.55	1.1	1.04	440
HNC ⁺ + N ₂ O → NO ⁺ + HNCN	0.45			
HCN ⁺ + O ₂ → O ₂ ⁺ + HCN	1.0	0.50	0.77	147
HNC ⁺ + O ₂ → HNC ⁺ + O	0.75	0.36	0.77	109
HNC ⁺ + O ₂ → NO ⁺ + HCO	0.25			

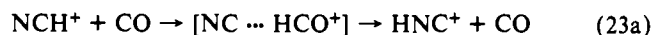
^aCollision rate coefficients derived from the Langevin expression for neutral reactants with no dipole moment or the variational transition state theory (ref 30). ^bHeats of formation have been estimated from the values tabulated in ref 12 except where stated otherwise in the text. ^cEstimated on the basis that Δ*H*_f(HNC⁺) = 1373 kJ mol⁻¹ from this work.

$k_{\text{reaction}} = k_{\text{L}} e^{-\Delta E/kT}$. Theoretical values are 993 kJ mol⁻¹²⁶ and 989 kJ mol⁻¹²⁷ so that probably reaction 21b is about 4 kJ mol⁻¹ endothermic, but within the present uncertainties it could be thermoneutral.

We might next consider why the near thermoneutral reaction between HOC⁺ and H₂ is more efficient at producing H₃⁺ than is the reaction between HCN⁺ and CO at producing the more exothermic HCO⁺ product. In both cases the first step of the isomerization reaction is the production of the proton transfer complex ions



and

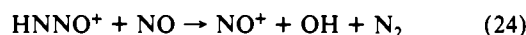


In reaction 22, the initial proton transfer is nearly thermoneutral and probably endothermic so that only a fraction of the collisions (perhaps as low as 1/3) produce (CO ... H₃⁺). As the polarizability of H₂ is very small (the situation before proton transfer occurs) and the dipole moment of CO (0.112 D) is also very small (the situation after proton transfer), then the electrostatic forces are relatively weak and in both cases quite isotropic. Perhaps the outcome of the reaction is then just a matter of more or less equal numbers of complexes having proper orientations for either proton transfer back to the CO carbon atom (yielding HCO⁺) or back to the OC oxygen atom (reforming HOC⁺). It is not possible, however, to decide what fraction of the nonreactive collisions (2/3 of the total collisions) involves proton transfer from H₃⁺ back to the O atom of CO (no apparent reaction) and what fraction represents the nonformation of an H₃⁺ ... CO complex in the initial collision due to endothermicity (no reaction).

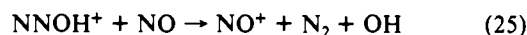
In the HCN⁺ + CO collision, reaction 23, the initial proton transfer (NC ... HCO⁺) is very exothermic (73 kJ mol⁻¹) so that NC and HCO⁺ in the complex have considerable internal energy with rotational and even vibrational components. Since CN has a large dipole moment (1.45 D) the CN and HCO⁺ moieties are

constrained in a deep electrostatic well with the result that the potential is very anisotropic. Thus after the initial proton transfer from the C atom of CN, the dipole is oriented in the wrong direction and will have a torque rotating it so as to point the negative N atom to approach the HCO⁺. Exothermic proton transfer from HCO⁺ to the N atom of NC will then occur and the results show that this is evidently a very efficient process.

The mechanism of "forth and back" hydrogen transfer has been invoked in earlier studies.^{19-21,28} Recently the seemingly improbable reaction



has been rationalized²⁸ as an exothermic proton transfer from N of N₂O to N of NO, followed by exothermic proton transfer back to O of N₂O, followed in turn by dissociative charge transfer



Reaction 25 is known from independent studies to be efficient.²⁹

Conclusions

Electron impact of 30-40 eV electrons on HCN results in a mixture of HCN⁺/HNC⁺ isomers which are readily distinguished in a flow tube on the basis of their reactivity with CF₄ and product distribution with SF₆. The apparent slow exothermic proton transfers of HCN⁺ with CO and CO₂ have been shown to lead to efficient isomerization of HCN⁺ to HNC⁺. The isomerization can be rationalized in terms of a "forth and back" mechanism for proton transfer within the complex. The production of HNC⁺ from the reaction of C₂N₂⁺ with HCN can also be accounted for by a similar mechanism which is facilitated by the anisotropic potential induced by the large dipole moment of CN.

Note Added in Proof. A recent reinvestigation of SF₅⁺ thermochemistry³¹ has shown that the value of AP(SF₅⁺/SF₆) = 13.98 ± 0.03 eV used in this paper is incorrect. This value was based

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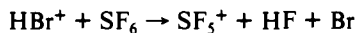
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on the determination of $IP(SF_5) \leq IP(NH_3) = 10.14 \text{ eV}^{14,32}$ but which has been shown subsequently to be too large. The corrected value $IP(SF_5) = 9.65 \pm 0.05 \text{ eV}^{31}$ leads to $AP(SF_5^+/SF_6) = 13.60 \text{ eV}$ and $\Delta H_f(SF_5^+) = 12 \text{ kJ mol}^{-1}$. This reduced value of $\Delta H_f(SF_5^+)$ was anticipated recently by the observation of the reaction



which has been reported by Tichy et al.³³ to proceed at the collision rate requiring $AP(SF_5^+/SF_6) < 13.87 \pm 0.04 \text{ eV}$. In consequence, reaction 1 reported here is more exothermic than indicated by the

ΔH values detailed in Table I and within the text: i.e., $\Delta H_1 = -49 \text{ kJ mol}^{-1}$.

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Formation and Fragmentation of Gas-Phase Titanium/Oxygen Cluster Positive Ions

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Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77204-5641. Received February 5, 1990. Revised Manuscript Received May 7, 1990

Abstract: Positive ions of titanium/oxygen clusters have been investigated with mass spectrometry and collision-induced dissociation. The cluster ions were produced by sputtering titanium dioxide powder and titanium foil (exposed to oxygen) with an energetic (8 keV) xenon atom beam. Titanium/oxygen cluster ions sputtered from the foil were seen to have the form $[Ti_nO_{2n-\delta}]^+$, where n equals 1 to 8 and δ ranges from 0 to 4. Sputtering titanium dioxide powder yields abundant $[Ti_nO_{2n-\delta}]^+$ clusters, where n equals 1 to 7 and $\delta = 1, 2, \text{ and } 3$. Titanium foil sputtered in a high-pressure (0.1–0.2 Torr) fast-atom bombardment (HPFAB) ion source with O_2 produces $[Ti_nO_{2n-1}]^+$ cluster ions as the only abundant cluster species. The collision-induced dissociation spectra of $[Ti_nO_{2n-\delta}]^+$ clusters show mainly losses of Ti, TiO, and TiO₂ moieties. Mass-selected $[Ti_nO_{2n-\delta}]^+$ cluster ions also react hyperthermally with O_2 in the collision quadrupole of a tandem mass spectrometer to form $[Ti_nO_{2n-1}]^+$ clusters. A simple pair-potential ionic model was used to calculate energy-optimized geometric structures of the clusters. Distinct structural differences between the Ti_nO_{2n-2} and Ti_nO_{2n-1} clusters were not found, whereas the lowest energy Ti_nO_{2n} isomers were found to have pendant and terminal oxygen atoms. For both titanium/oxygen and cobalt/oxygen clusters, the pair-potential model identifies the most abundant clusters as those having the lowest calculated energy per atom.

Introduction

There is tremendous interest in characterizing the chemistry of gas-phase metal/oxygen ions¹⁻⁵ and clusters.⁶⁻⁸ An early study of gas-phase metal cluster reactions reported the reactivity of Mn_2^+ with O_2 to form Mn^+ , MnO^+ , and Mn_2O^+ .⁹ Anderson and co-workers¹⁰⁻¹² as well as Jarrold and Bower¹³⁻¹⁵ have studied the reactions of Al_n^+ clusters with O_2 . The reactions of Cu_n^+ clusters with O_2 have been studied with FTMS.¹⁶ The reactions of homo- and heterogeneous di- and trimethyl cobalt and iron ions with O_2 have been studied with FTMS.¹⁷ In this latter study, the cluster ions were formed by electron ionization of the corresponding volatile metal carbonyl followed by multistep reaction sequences to form the desired precursor(s). Thermochemical data from these studies suggest the formation of bridged oxide species for $[M'MO]^+$, $[M'MO_2]^+$, and $[M'M_2O_3]^+$ ($M, M' = Fe, Co$). Thus, the role of structure in determining the reactivity of metal/oxygen cluster ions needs to be addressed. To answer that question, the types and structures of metal/oxygen cluster ions that can be produced must be determined.

We have previously reported studies of the formation, fragmentation, and reactions of cobalt/oxygen cluster ions.^{18,19} The cluster ions were formed by sputtering Co in the presence of O_2 (0.1 Torr). Two major classes of cluster ions were observed: $[Co_nO_{n-1}]^+$ and $[Co_nO_n]^+$. Collision-induced dissociation (CID) was used to obtain structural information for the cobalt/oxygen cluster ions.¹⁸ In general, the fragment ions produced had the stoichiometry $[Co_nO_x]^+$. This corresponds to losses of Co_yO_y ($y = 1-3$) from the $[Co_nO_n]^+$ clusters and to losses of Co_yO_{y-1} ($y = 1-3$) from the $[Co_nO_{n-1}]^+$ clusters. Geometric structures of

the cobalt/oxygen cluster ions were calculated with use of a simple Coulomb plus Born-Mayer pair-potential model. The Co_nO_{n-1}

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