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Carbene-like Character of Gaseous Ions. An Ion Cyclotron Resonance and ab Initio Investigation of the Reactions of Difluoronitrenium Ion with Methane

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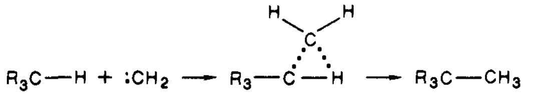
Abstract: The details of the reaction of difluoronitrenium ion, NF_2^+, with methane have been explored using pulsed ion cyclotron resonance, pulsed ionization high-pressure mass spectrometric, and collision-induced decomposition experiments. The NF_2^+ ion which is isoelectronic with difluorocarbene, CF_2, appears to insert very readily into the C–H bond of methane, and the newly formed adduct ion subsequently loses two molecules of HF generating nitrogen-protonated hydrogen cyanide, $HCNH^+$. The structure of this product ion has been confirmed using CID experiments and energetic arguments based on ab initio calculations. A proposed potential energy surface for the reaction has been investigated using ab initio techniques to calculate energies of reaction intermediates and transition states. Indirect evidence for a $CH_3NF_2H^+$ intermediate has been obtained from the high-pressure mass spectrometric experiments. Protonated NF_3 is also found to react to produce $HCNH^+$, which is consistent with a fluorine protonated structure. The relative energies of HNF_3^+ and F_2NFH^+ have been examined using large basis set ab initio calculations which confirm slightly greater stability of the fluorine protonated form. Evidence for the presence of a triplet state of NF_2^+ is also presented.

The use of mass spectrometric techniques for the investigation of mechanistic details of gas-phase ion molecule reactions has been abundantly demonstrated.[1-4] In addition, ab initio methods[5,6] have recently been applied to such systems to probe more readily the nature of the potential energy surface for gaseous ionic reactions as well as the energetics and geometries of reactants, products, and transition states. One of the most extensively studied types of reaction in traditional physical organic chemistry has been the bond insertion chemistry of carbenes and "carbene-like" species.[7,8] Two mechanisms have been proposed for insertion of the parent carbene, methylene ($:CH_2$), into C–H bonds. The first of these, direct insertion, involves a concerted process of bond breakage and formation via a three-center transition state:[9]



$$R_3C{-}H + :CH_2 \rightarrow R_3{-}\overset{CH_2}{C}{\cdots}H \rightarrow R_3C{-}CH_3 \quad (1)$$

The second, abstraction–recombination, is a two-step process is which initial end-on attack of the C–H bond by the carbene resulting in formation of two radicals is followed by radical recombination to yield the final product:[10]

$$R_3C\text{-}H + :CH_2 \rightarrow R_3C^{\cdot} + CH_3^{\cdot} \rightarrow R_3CCH_3 \quad (2)$$

In an early Hückel MO study of methylene insertion into the C–H bond of methane, Hoffmann[11] concluded that the approach of $:CH_2$ to CH_4 occurs on an "abstraction-like" path, in support of a suggestion by Benson;[10] however, no actual abstraction occurs and the reaction proceeds subsequently via a three-center structure leading to the C_2H_6 production.

Kollmar[12] has suggested that the insertion reaction proceeds in two stages with electrophilic attack by the empty p orbital of the methylene carbon on the C–H bond followed by nucleophilic interaction of the methylene lone pair with a C–H antibonding orbital.

Most recently, Gordon[13] has examined the $:CH_2$–CH_4 potential energy surface using ab initio methods. At the 3-21G and 6-31G* basis set levels, insertion of methylene into the methane C–H bond is found to proceed through a transition state with a 9 kcal mol^{-1} barrier height. However, when correlation effects are included (MP3/6-31G*//3-21G), this barrier completely disappears. In this examination of the potential energy surface it was found that the minimum energy pathway involved approach with a large C–H–C angle (128°) before proceeding to the three-center transition-state structure. Thus the reaction resembles an abstraction in its early stages, also in qualitative agreement with the suggestions by Benson.[10]

Hoffmann[14] has recently advanced the principle of isolobality as a means of understanding the electronic structure and reactivity of compounds. Two species are said to be isolobal if they have similar number, symmetry properties, approximate energies, and occupation by electrons of their frontier orbitals. If this is the case, similar reactivity might then also be expected. On this basis, it is instructive to reinterpret the reactions of gaseous ions which are isolobal (and isoelectronic) with carbenes. For example, Cross and co-workers[15] have investigated the reactions of NH_2^+ with methane in a crossed beam apparatus and, using isotopic labeling, found that eq 3 proceeds via a combination of two or more

$$NH_2^+ + CH_4 \rightarrow CH_2NH_2^+ + H_2 \quad (3)$$

mechanisms. The proposed mechanisms include the formation of an ammonium ion ($CH_3NH_3^+$) intermediate, which, although the authors do not specifically mention it, is consistent with an insertion process by NH_2^+ which is isoelectronic and isolobal with $:CH_2$. The occurrence of other major reaction channels, however,

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[†] E. W. R. Steacie Fellow, 1986–1988.

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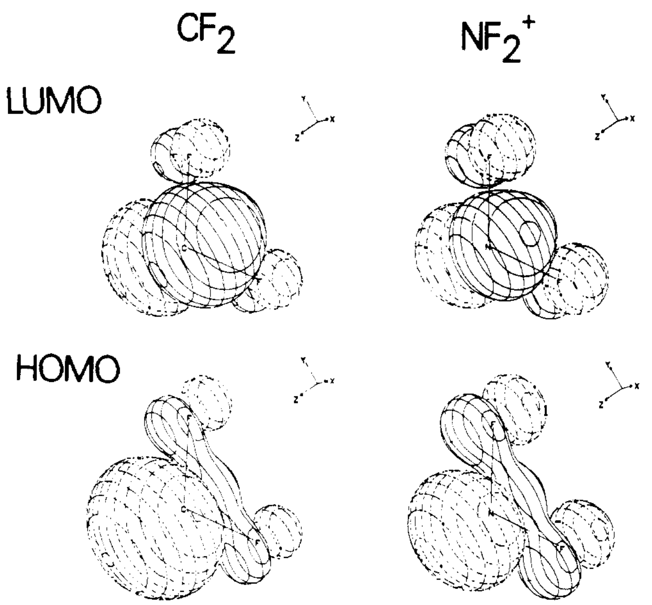

Figure 1. Molecular orbital contour plots for the HOMO and LUMO of CF_2 and NF_2^+.

precludes more incisive deductions on the details of a possible insertion reaction.

Difluoromethylene has been one of the most extensively studied of the halocarbenes.[16] However, to date, no attention has been focused on the gas-phase ion chemistry of its isoelectronic analogue, the difluoronitrenium ion, NF_2^+. As illustrated by the molecular orbital plots in Figure 1,[17] the frontier orbitals of these two species are sufficiently similar in shape, symmetry, and relative energies to satisfy the isolobal analogy criteria. Thus it might be expected that NF_2^+ would also exhibit carbene-like character in its reactions with species where C–H bond insertion is possible. In the present manuscript we wish to report the results of investigations of the gas-phase ion chemistry in NF_3–CH_4 mixtures using the techniques of ion cyclotron resonance spectroscopy, high-pressure mass spectrometry, and collision-induced decomposition on a reversed geometry double focusing mass spectrometer. In addition mechanistic proposals have been elucidated with the aid of the ab initio calculations.

Experimental Section

Pulsed ion cyclotron resonance (ICR) experiments were carried out at ambient temperature (25 °C) in an instrument of dual region cell design operating in both drift and trapped ion modes.[18] Frequency swept detection was accomplished using a capacitance bridge detector of Wronka-Ridge design.[19] All details of pulsed ion cyclotron resonance spectroscopy have been described in detail previously.[20]

Pulsed ionization high-pressure mass spectrometric (HPMS) experiments were performed on an instrument recently constructed at the University of Waterloo.[21] High-pressure mass spectrometric techniques have also been recently reviewed.[22]

Collision-induced decompositions of magnetically mass selected ions (CID-MIKES) were investigated on VG instruments ZAB 2F BEQQ spectrometer at the Ontario Regional Ion Chemistry Laboratory at the University of Toronto.[23]

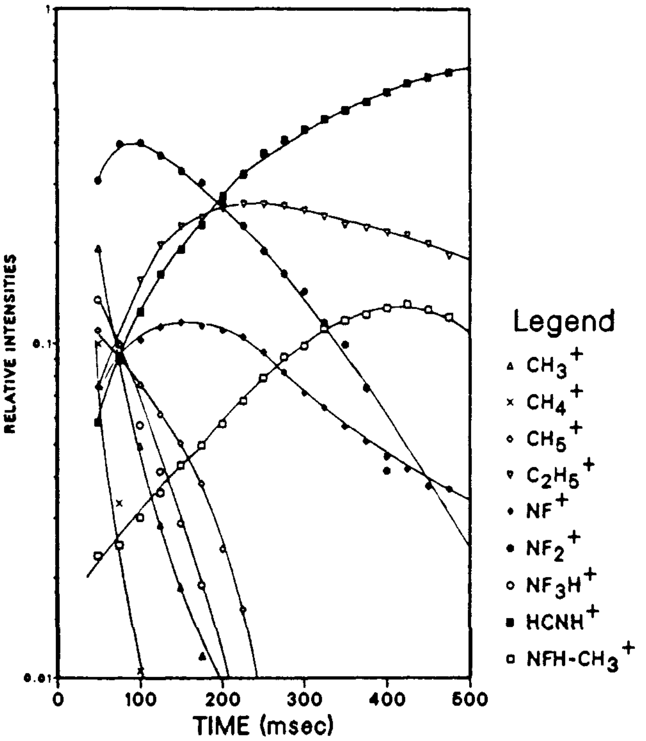

Figure 2. Variation of ICR ion intensities with time following a 5-ms, 70-eV electron beam pulse in a 1:1 mixture of NF_3/CH_4 at a total pressure of 1.2×10^{-6} Torr.

Ab initio calculations were done with the Gaussian 82 program package.[24] All calculations were carried out initially at the 3-21G basis set level. For NF_3H^+ where accurate energetics were required, optimization was done at the 6-31G** level.

Nitrogen trifluoride was obtained from Ozark Mahoning Inc., methane from Matheson Canada Ltd., and methane-d_4 from Merck Sharpe and Dohme Canada Ltd. All materials were used without further purification.

Results and Discussion

The present investigation of the gas-phase ion chemistry of NF_3/CH_4 mixtures was provoked by failure of attempts to determine the proton affinity of NF_3 in HPMS experiments using CH_4 as the major bath gas. In these experiments the only persistent species of appreciable abundance observed after the initial ionization pulse were ions of m/z 28 and 29. The possible ions at m/z 28 are N_2^+, CO^+, $C_2H_4^+$, and CH_2N^+, and, of these, the first three, being radical cations, would not be expected to be persistent in the presence of CH_4. Further, the use of NF_3/CD_4 mixtures resulted in persistent species at m/z 30 and 34, establishing the presence of two hydrogens in the lower molecular weight ion. Thus it was established that the persistent species at m/z 28 had the molecular formula CH_2N^+. It was initially considered that this ion might arise from the presence of HCN as an impurity in the NF_3/CH_4 mixture. However, the failure to observe reaction 4 ruled out this possibility since proton transfer from $C_2H_5^+$ to

$$C_2H_5^+ + HCN \rightarrow HCNH^+ + C_2H_4 \qquad (4)$$

HCN is known to be exothermic and would proceed rapidly.

In order to determine the origin of this species at m/z 28, mixtures of NF_3 and CH_4 were examined using ion cyclotron resonance spectroscopy. The only previous account of observations in this mixture reported only the occurrence of proton transfer, eq 5.[25] The variation of ICR ion intensities with time in a 1:1

$$CH_5^+ + NF_3 \rightarrow NF_3H^+ + CH_4 \qquad (5)$$

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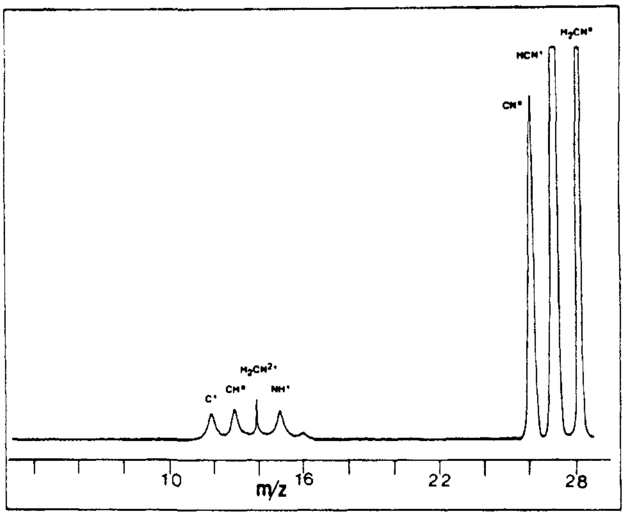


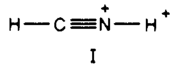
Figure 3. CID-MIKES spectrum of m/z 28 derived from chemical ionization of a 10:1 NF_3/CH_4 mixture.

mixture of NF_3/CH_4 is shown in Figure 2. It is immediately evident that, as seen in the earlier HPMS experiments, m/z 28 dominates the ion chemistry at long reaction time. Experiments with CD_4 lead to a shift in the major ion to m/z 30 as seen in the HPMS result. Double resonance experiments establish that this product ion is the result of reaction of both NF_2^+ and NF_3H^+ with CH_4:

$$NF_2^+ + CH_4 \rightarrow CH_2N^+ + 2HF \quad (6)$$

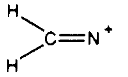
$$NF_3H^+ + CH_4 \rightarrow CH_2N^+ + 3HF \quad (7)$$

These reactions in which two and three molecules of HF are eliminated seem initially somewhat difficult to comprehend. In order to understand more thoroughly the nature of these reactions, it is important to know the structure of the CH_2N^+ ionic product. The three possible ion structures, I–III, have been examined by

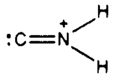


$$H{-}C{\equiv}\overset{+}{N}{-}H^+$$

I



II

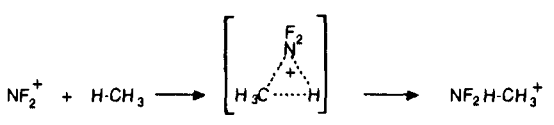


III

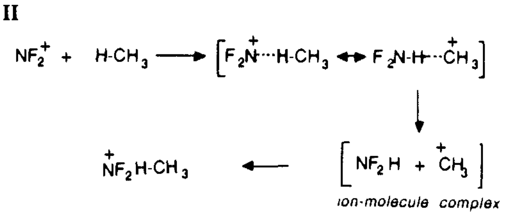
ab initio calculation by both DeFrees and McLean[26] and by Schaefer.[27] They find that nitrogen protonated HNC, III, is 46 kcal mol^{-1} higher in energy than I. Carbon protonated HCN, II, is found to be a saddle point on the CH_2N^+ surface in the singlet state lying 72 kcal mol^{-1} above I in energy. A minimum corresponding to a triplet state of II is also found; however, it lies ~120 kcal mol^{-1} above I. Thus I is by far the lowest energy structure and it is mechanistically more probable than III. Further if II is produced as a bound triplet state of high energy, it might then be expected to react by proton transfer which is not observed. It was therefore concluded on the basis of these energetics data that the structure of the m/z 28 formed in eq 6 and 7 is most likely nitrogen protonated HCN, I.

To probe further the structure of this ion, mixtures of NF_3 and CH_4 were examined using the chemical ionization source of a reversed geometry double-focusing mass spectrometer. The collision-induced decomposition spectrum (CID-MIKES) of the m/z 28 ion derived from this mixture is shown in Figure 3. The m/z 12–16 region is found to agree nearly exactly with that observed by Holmes et al.[28] for CID of m/z 28 produced by proton transfer from H_3O^+ to HCN. Further, this spectrum is significantly different from that of CH_2N^+ produced by charge inversion of CH_2N^- and that of CNH_2^+ derived from CD_3NH_2. The collision-induced decomposition experiments therefore also support the structure of the ion at m/z 28 produced in NF_3/CH_4 mixtures as nitrogen protonated HCN, I.

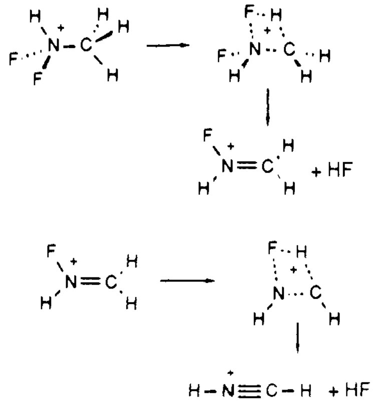
Scheme I



Scheme II



Scheme III



Taking the structure of m/z 28 as I, a mechanism must then be proposed for eq 6 and 7 whereby three C–H bonds are broken, a new C–N bond is made, a new N–H bond is made, and either two or three molecules of HF are lost. Given the isoelectronic and isolobal nature of NF_2^+ and CF_2, it is logical to propose that eq 6 proceeds via a C–H bond insertion of NF_2^+ into CH_4. By analogy to carbene chemistry this will occur either by a direct insertion mechanism, Scheme I, leading to a three-center-two electron bond intermediate, which rearranges to $CH_3NF_2H^+$, or via an "abstraction-like" mechanism, Scheme II, in which hydride transfer occurs to yield an ion–molecule complex, sufficiently long lived to undergo recombination to $CH_3NF_2H^+$. On the basis of thermochemical data, hydride extraction from CH_4 by NF_2^+ is seen to be exothermic, making Scheme II a plausible mechanism. Significantly, dihalocarbenes in singlet states are frequently observed to react via the abstraction–recombination mechanism, and, in fact, it has also been proposed that reaction of dichlorocarbene with C–H bonds may proceed by a hydride abstraction–recombination mechanism, eq 8.[29] Whatever the mechanism for its

$$R_3C\text{-}H + :CCl_2 \rightarrow [R_3C^+ + {}^-CHCl_2] \rightarrow R_3CCHCl_2 \quad (8)$$

production, the resulting protonated *N,N*-difluoromethylamine will contain considerable internal excitation, enabling it to undergo sequential unimolecular losses of HF to yield the nitrogen protonated HCN, as outlined in Scheme III.

In order to determine whether $CH_3NF_2H^+$ was indeed an intermediate in the production of $HCNH^+$, a high-pressure mass spectometric experiment was carried out using N_2 as the major bath gas to which small amounts of CD_4 and NF_3 were added. It was felt that in such a mixture the initially formed $CD_3NF_2D^+$ might be collisionally stabilized by N_2, eq 9, thus preventing

$$NF_2^+ + CD_4 \rightarrow [CD_3NF_2D^+]^* \xrightarrow{N_2} CD_3NF_2D^+ \quad (9)$$

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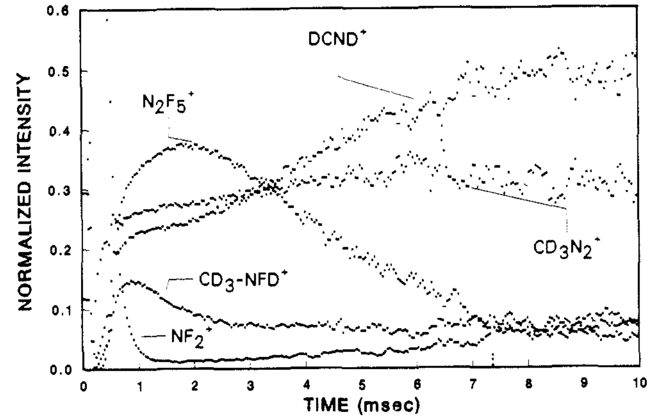

Figure 4. Variation of HPMS ion intensities with time following a 50-ms electron beam pulse in an $NF_2/NF_3/CH_4$ mixture (N_2, 5 Torr; NF_3, 5 mTorr; CH_4, 5 mTorr).

unimolecular loss of HF and permitting the direct observation of the association product, protonated *N*,*N*-difluoromethylamine. The results of this experiment, shown in Figure 4, reveal that no collisionally stabilized $CD_3NF_2D^+$ is produced; however, another major product, $CD_3N_2^+$, is observed which provides indirect evidence for the formation of $CD_3NF_2D^+$. The time between collisions of ions with the bath gas in the HPMS ion source at ~5 Torr is on the order of 1–10 ns. Thus any species which is capable of undergoing exothermic reaction with the bath gas will not be observed. From these data it appears that some species, capable of transferring CD_3^+ to N_2, is produced as an intermediate but, since the time between collisions with the bath gas is so short, this species is not observed. A probable candidate for such a species is $CD_3NF_2D^+$, eq 10, with the conclusion that the methyl

$$CD_3NF_2D^+ + N_2 \rightarrow CD_3N_2 + NF_2D \qquad (10)$$

cation affinity of N_2 is greater than that of NF_2H.[30] Since both $CD_3N_2^+$ and $DCND^+$ are observed, it is probable that the lifetime of the activated $CD_3NF_2D^+$ toward unimolecular loss of HF is of the same order of magnitude as the time between collisions of ions with N_2 (~5 ns). Both $DCND^+$ and $CD_3N_2^+$ are seen to have a bimodal intensity distribution with reaction time. The initial increase evidently corresponds to direct reaction of NF_2^+ with CD_4 while the increase in $CD_3N_2^+$ and $DCND^+$ at later times appears to result from $N_2F_5^+$, eq 12, which is formed by clustering of NF_2^+ on NF_3, eq 11. It is also apparent that the NF_2+ binding energy to NF_3 is greater than that to N_2 since difluoronitrenium transfer, eq 13, is not seen.

$$NF_2^+ + NF_3 \xrightarrow{N_2} N_2F_5^+ \qquad (11)$$

$$N_2F_5^+ + CD_4 \rightarrow \begin{cases} DCND^+ + NF_3 + 2DF \\ CD_3N_2^+ + NF_2D \end{cases}$$

$$N_2F_5^+ + N_2 \rightarrow F_2NN_2^+ + NF_3 \qquad (12)$$

In order to test further the validity of the mechanism outlined in Scheme III ab initio calculations were carried out for the reactants, products and proposed intermediates and transition states. All structures were optimized at the 3-21G basis set level. In the case of transition states a skewed four-center structure was presumed and a saddle point located using the Berny optimization routine.[24] In the interest of cost, no higher level calculations were done since only the qualitative features of the potential energy surface were sought. The energy obtained for each of the relevant species is outlined in Table I and the structures are summarized in Figure 5. These data allow the construction of the potential energy surface for the reaction of NF_2^+ with CH_4 shown in Figure 6. It is noteworthy that each of the proposed intermediates lies at lower energy than its precursor and that each of the transition states, although lying higher in energy than the preceding intermediate, is lower than the total energy of the reactants. Thus the course of the reaction via the proposed mechanism is always energetically downhill. The total energy change calculated for eq 6 of −177 kcal mol^{-1} is in good agreement with the enthalpy change of −165 kcal mol^{-1} determined from experimental thermochemical data, lending confidence to the qualitative overall features of the potential energy surface.

The various mass spectrometric and ab initio data therefore combine to make Scheme III an extremely plausible mechanism for the generation of *m*/*z* 28 by reaction of NF_2^+ with CH_4. However, ion cyclotron double resonance experiments also showed that *m*/*z* 72, NF_3H^+, gives rise to *m*/*z* 28 in NF_3/CH_4 mixtures. In order to understand the mechanism by which protonated NF_3 reacts with methane to yield protonated HCN, it is necessary to first understand the structure of the NF_3H^+ ion. The two most probable structures are the nitrogen protonated form, IV, and the

Table I. 3-21G//3-21G Energies (au) of Relevant Species for the NF_3/CH_4 System

species	energy (au)	species	energy (au)
NF_3	-350.6327	CH_2NFH^+	-192.0692
CH_4	-39.9769	CH_2NFH^+ (T.S.)	-191.9382
HF	-99.4602	$HCNH^+$	-92.6456
NF_2^+	-251.3077	HNF_3^+ (IV)	-350.8354
$CH_3NF_2H^+$	-291.4839	F_2NFH^+ (V)	-350.8255
$CH_3NF_2H^+$ (T.S.)	-291.3447		

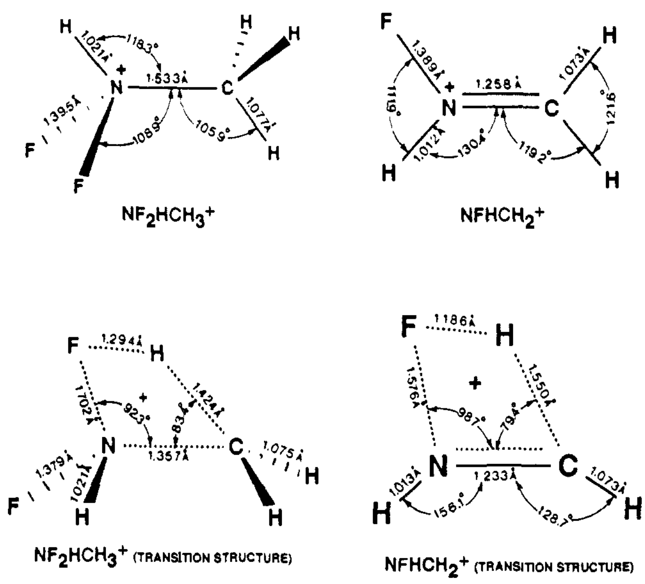

Figure 5. Structures of intermediates and transition states proposed for the reaction of NF_2^+ with CH_4 as outlined in Scheme III.

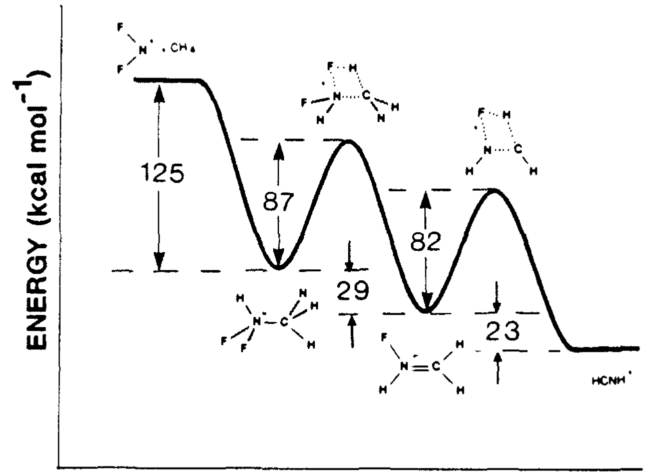

Figure 6. Ab initio potential energy surface for the reaction of NF_2^+ with CH_4.

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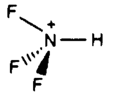
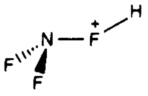
(30) McMahon, T. B.; Heinis, T.; Nicol, G.; Hovey, J. K.; Kebarle, P., *J. Am. Chem. Soc.*, preceding paper in this issue.

fluorine protonated form, V. In order to distinguish between these



IV



V

two possibilities an ICR experiment was devised in which the protonated NF_3 was reacted with n-donor bases whose proton affinities were less than that of NF_3. For CO_2 and HCl, where proton transfer, eq 13 and 14 is endothermic, nucleophilic displacement reactions were observed to occur in which HF is displaced by CO_2 and HCl, respectively, eq 15 and 16. These latter two reactions are reminiscent of the behavior of fluorine protonated methyl fluoride, CH_3FH^+, where a variety of weak bases, B (including Kr and Xe),[31,32] are able to displace HF from CH_3^+, eq 17. Thus the reactivity of NF_3H^+ toward the n-donor bases CO_2 and HCl, as well as the σ-donor base CH_4 suggests that fluorine protonation is more probable than nitrogen protonation.

$$NF_3H^+ + CO_2 \rightarrow CO_2H^+ + NF_3 \qquad (13)$$

$$NF_3H^+ + HCl \rightarrow H_2Cl^+ + NF_3 \qquad (14)$$

$$NF_3H^+ + CO_2 \rightarrow CO_2 \rightarrow CO_2NF_2^+ + HF \qquad (15)$$

$$NF_3H^+ + HCl \rightarrow HClNF_2^+ + HF \qquad (16)$$

$$CH_3FH^+ + B \rightarrow CH_3B^+ + HF \qquad (17)$$

Additional structural evidence for NF_3H^+ was obtained from a CID-MIKES experiment for m/z 72 derived from proton transfer chemical ionization of NF_3. The CID-MIKES spectrum, shown in Figure 7, reveals a dominant loss of HF, virtually no losses of either H or F, and the presence of a small HF^+ peak. This spectrum is thus also strongly suggestive of a fluorine protonated structure in which the weak F_2N^+–FH is most readily broken in a simple cleavage process under CID conditions.

No ab initio calculations had previously been performed on the two possible structures of NF_3H^+; however, the relative energies of nitrogen and fluorine protonated NH_2F have been examined by Pople et al.[33] At the 6-31G* basis set level the nitrogen protonated form is found to be favored by 40.6 kcal mol^{-1} over the fluorine protonated structure. However, with increasing replacement of hydrogens by fluorine, it would be expected that the nitrogen lone pair basicity would be decreased much more than that of the fluorine. As seen from the data in Table I, at the 3-21G basis set level nitrogen protonated NF_3 is only favored by 6 kcal mol^{-1}, consistent with this prediction. In order to assess whether improved basis sets would lead to fluorine protonation being more favorable, a complete geometry optimization of both IV and V as well as NF_3 was carried out at the 6-31G** level. In addition, harmonic vibrational frequencies were determined for all three species to permit zero-point energy corrections, as well as the thermal contributions to the proton affinity. The calculated electronic energies and zero-point energies of NF_3 and the two forms of protonated NF_3 are summarized in Table II and the structures are given in Figure 8. The data for NF_3 and HNF_3^+ are in excellent agreement with values obtained by Schleyer at the 6-31G* level.[34] From these data it can be seen that at the 6-31G** level, although the electronic energy of HNF_3^+ (IV) is 2 kcal mol^{-1} below that of F_2N–FH^+ (V), after the zero-point energy correction is made the fluorine protonated form is 2.2 kcal mol^{-1} energetically more favorable than the nitrogen protonated form. In addition the calculated proton affinity at the 6-31G** level of 139.8 kcal mol^{-1} is in excellent agreement with the experimental value of 140.7 kcal mol^{-1}.[35]

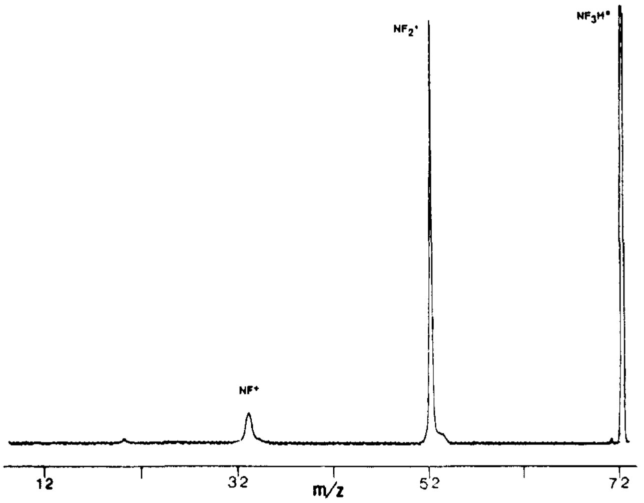


Figure 7. CID-MIKES spectrum of m/z 72 derived from a 10:1, NF_3/CH_4 mixture.

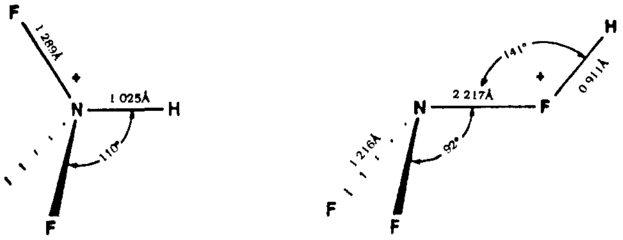


Figure 8. 6-31G** optimized geometries for HNF_3^+ and F_2NFH^1.

Table II. 6-31G**//6-31G** Energies and Zero-Point Energies of NF_3, HNF_3^+, and F_2NFH^+

species	energy (au)	ZPE (kcal mol^{-1})[a]
NF_3	−352.5401	7.2
HNF_3^+	−352.7714	16.3
F_2NFH^+	−352.7682	12.0

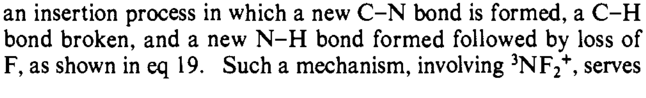
[a] Zero-point energies calculated from a summation of vibrational frequencies have been scaled by a factor of 0.9 to give the tabulated values: DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

Accepting that the structure of at least the reactive form of NF_3H^+ is a difluoronitrenium ion weakly bound to a molecule of HF, the mechanism for production of protonated HCN can be readily understood as a simple NF_2^+ transfer from HF to CH_4 followed by sequential losses of HF from the initially formed complex just as in Scheme III for NF_2^+.

The major remaining unexplained feature in the gas-phase ion chemistry of NF_3/CH_4 mixtures is the ion of m/z 49 which becomes m/z 53 in NF_3/CD_4 mixtures. This isotopic shift establishes the molecular formula of hydrogen-containing species as CH_4NF^+, a radical cation. Double resonance experiments establish that this species arises from NF_2^+ (eq 18), a reaction

$$NF_2^+ + CH_4 \rightarrow CH_4NF^+ + F \qquad (18)$$

in which a nominally closed-shell cation reacts with a closed-shell neutral to yield a pair of radical products. This leads to the possibility that while $HCNH^+$ arises from reaction of singlet NF_2^+ the minor product, CH_4NF^+, is the result of triplet NF_2^+. A possible mechanism for reaction of $^3NF_2^+$ with CH_4 is again via an insertion process in which a new C–N bond is formed, a C–H bond broken, and a new N–H bond formed followed by loss of F, as shown in eq 19. Such a mechanism, involving $^3NF_2^+$, serves



$$^3NF_2^+ + CH_4 \rightarrow H_3C\cdots H(NF_2^+) \rightarrow CH_3NF_2H^{+*} \rightarrow CH_3NFH^{+\cdot} + F \qquad (19)$$

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to explain the otherwise rare occurrence of a radical cation and neutral resulting from closed-shell ion and neutral reactants. The CID-MIKES spectrum of this ion also supports the structure proposed above. Cleavage of the C–N bond results in peaks of comparable intensity at *m/z* 15 (CH_3^+) and *m/z* 34 (NFH^+). Loss of HF + H results in a broad major peak at *m/z* 28 ($HCNH^+$) with smaller contribution at *m/z* (H_2CNH^+) from loss of HF and *m/z* 27 (HCN^+) from loss of HF + H_2.

Further experiments are planned to attempt to generate selectively $^3NF_2^+$ to establish the different reactivity of the possible electronic states of the difluoronitrenium ion.

Conclusion

Ion cyclotron resonance, high-pressure mass spectrometric, and collision-induced decomposition experiments as well as ab initio calculations have been used to investigate the gas-phase ion–molecule reactions occurring in nitrogen trifluoride–methane mixtures. The major feature of this chemistry is the production of nitrogen protonated hydrogen cyanide from the reaction of both NF_2^+ and NF_3H^+ with methane. In the former case a probable mechanism involving C–H bond insertion of the carbene-like cation NF_2^+ has been proposed consistent with each of the types of experimental data obtained. Protonated NF_3 has been strongly suggested to be a fluorine protonated species which reacts via NF_2^+ transfer to CH_4 in a manner exactly analogous to that of naked NF_2^+. The potential energy surface has been qualitatively explored using ab initio calculations which show that the proposed intermediates and transition states are energetically feasible. A difference in reactivity of $^1NF_2^+$ and $^3NF_2^+$ has been proposed based on the appearance of a radical cation product, CH_3NFH^+.

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Gas-Phase Lewis Acid–Base Interactions. An Experimental Determination of Cyanide Binding Energies from Ion Cyclotron Resonance and High-Pressure Mass Spectrometric Equilibrium Measurements

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Abstract: Both ion cyclotron resonance and high-pressure mass spectrometric equilibrium techniques have been used to investigate the binding energies of anions to a variety of Lewis acids. From an analysis of the enthalpy changes associated with CN^- binding it is evident that in cases of relatively weak binding considerable freedom of rotational motion of CN^- in the complex may be retained. Ab initio calculations and experiment suggest that binding through both the N and C sites of CN^- is nearly equally favorable in some cases. In contrast to results previously obtained for Brønsted acids which showed that CN^- and Cl^- bind nearly identically, the present data for Lewis acids show many cases where cyanide is much more favorably bound than chloride, a consequence of enhanced covalent binding of the CN^- complexes. New Kroeger Drago parameters derived for CN^- support the importance of covalent binding in cyanide adducts. Correlations of binding energy of anions to Lewis acids with the anion proton affinity show excellent linear relationships which may be used to predict binding energetics for new anions.

Since the introduction by Lewis of the electron pair acceptor–electron pair donor definition of acids and bases,[1] chemists have attempted to develop quantitative Lewis acidity and basicity scales. These attempts have been largely frustrated by the failure of a given series of Lewis acids to display the same qualitative order of binding strength toward different bases. The realization that such a constant ordering of strengths is not possible came as an outgrowth of a better understanding of bonding interactions.[2] As a result, in 1965 Drago and Wayland[3] formulated an equation predicting acid–base interaction energetics based on the ability of both acid and base to participate in electrostatic and covalent interactions. From examination of a large number of interactions, *E* (electrostatic) and *C* (covalent) parameters were assigned to species such that the strength of interaction between acid (A) and base (B) is given by eq 1. A similar, more qualitative theory,

$$-\Delta H_{\text{A-B}} = E_A E_B + C_A C_B \qquad (1)$$

the hard–soft Acid–Base (HSAB) principle, was advanced at roughly the same time by Pearson,[4] in which acids and bases were classified as either "hard" or "soft" with the general formalism that hard–hard or soft–soft acid–base interactions are more favorable than hard–soft interactions. In effect this principle also recognizes the simple idea that individual electrostatic and covalent interactions are highly idiosyncratic.

Each of these, and similar, theories suffers from the significant disadvantage that they are formulated largely on the basis of solution-phase interactions. Thus interactions of species, particularly ionic ones, with solvent can disguise the magnitude of interaction of that species with its acid or base substrate counterpart. For this reason gas-phase acid–base interaction energetics are particularly valuable since the intrinsic, electronic nature of

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