Inorg. Chem. **1995,** *34,* 1325−1332

Gaseous Fluorodiazonium Ions. Experimental and Theoretical Study on Formation and Structure of FN_2^+

Fulvio Cacace,[†] Felice Grandinetti,*,[‡] and Federico Pepi[†]

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Universitá di Roma "La Sapienza", P.le A. Moro 5, 00185 Rome, Italy, and Dipartimento di Scienze Ambientali, Universitá della Tuscia, Via S. C. De Lellis, 01100 Viterbo, Italy

Received June 3, 1994[®]

Gaseous fluorodiazonium ions, FN_2^+, have been successfully obtained from the ionization of NF_3/HN_3 mixtures under typical chemical ionization (CI) conditions. Using ^{15}N-labeled hydrazoic acid, the formation of $FN^{15}N^+$ ions is detected. The collisionally activated dissociation (CAD) experiments performed to probe the structures of FN_2^+ and $FN^{15}N^+$ indicate that, in the latter species, the two nitrogen atoms are not structurally equivalent. Thus, it is legitimate to identify the FN_2^+ ions as the linear $F{-}N{-}N^+$, invariably predicted by all the available theoretical studies as the global minimum on the potential energy surface. The mechanism of formation of the fluorodiazonium ions has been investigated by mass-analyzed ion kinetic energy (MIKE) and Fourier-transform ion cyclotron resonance (FT-ICR) spectrometry, as well as by post-SCF ab initio calculations, up to the GAUSSIAN-1 level of theory. The FN_2^+ ions originate from the loss of HF from a $F_2N{-}NH^+$ moiety, detected as well in the CI plasma and structurally characterized by CAD spectrometry. The details of this unimolecular decomposition have been enlightened by combining the evidence from the MIKE experiments and the results of the GAUSSIAN-1 ab initio calculations. The ion−molecule reactions following the ionization of the NF_3/HN_3 mixtures have been also investigated by FT-ICR. In the low-pressure domain typical of these experiments, the gas-phase ion chemistry essentially consists of the fast electron transfer reactions from HN_3 to $NF_3^{\bullet+}$, NF_2^+, and $NF^{\bullet+}$. Protonated hydrazoic acid, $H_2N_3^+$, is eventually observed as the dominating species at long reaction times.

Introduction

The fluorodiazonium ion, FN_2^+, is a species of considerable fundamental interest.[1−16] Since 1965, when Moy and Young[1] first reported the reaction of *cis*-difluorodiazine with arsenic pentafluoride to form a white solid adduct assigned as $FN_2^+AsF_6^-$

$$cis\text{-}F_2N_2 + AsF_5 \rightarrow FN_2^+AsF_6^-$$

the structure, bonding, and properties of the previously unknown FN_2^+ ion have been extensively investigated by X-ray diffraction, NMR, IR, Raman, and millimeter-wave spectroscopy,[1−6,8,9,13,16] as well as by theoretical methods.[7,10−12,14−16] As a result, the peculiar role of the FN_2^+ cation in the chemistry of the compounds containing nitrogen−fluorine bonds is currently well recognized.

The most interesting structural feature of the FN_2^+ ion is the small N−F bond length. In keeping with previous force field[6] and ab initio calculations,[7,11,12] the recently reported value of 1.22 Å, based on a combined X-ray diffraction and theoretical study,[13] is by far the shortest distance observed to date for any N−F bond.[17] This finding is consistent with the results of an independent investigation, based on high-resolution millimeter-wave spectroscopy and high-level theoretical calculations,[16] which furnish 1.2461 Å for the N−F bond length of the isolated FN_2^+ cation. The nitrogen−nitrogen bond distance of FN_2^+ is also of interest. Its observed value of 1.099 Å[13] is comparable to those of 1.0976 Å in N_2[18] and 1.118 Å in $N_2^{\bullet+}$ [19] and supports the triple character of the N−N bond of FN_2^+, which justifies the conclusion of Christe et al.[13] that "the FN_2^+ cation is highly unusual". In addition, the $^{14}N{-}^{19}F$ coupling constant of FN_2^+, measured by ^{14}N[8] and ^{19}F[1] NMR spectroscopy, is as large as 339 Hz, the highest $J(^{14}N{-}^{19}F)$ value reported to date. All these structural evidences have been rationalized[8,13] in terms of the high s character of the nitrogen bonding orbitals of FN_2^+.

The fluorodiazonium ion is one of the few non-benzenoid diazonium ions actually observed in solution,[20] and in view of

---

[†] Universitá di Roma "La Sapienza".

[‡] Universitá della Tuscia, Viterbo.

[®] Abstract published in *Advance ACS Abstracts,* January 1, 1995.

(1) Moy, D.; Young, A. R., II. *J. Am. Chem. Soc.* **1965**, *87*, 1889.

(2) (a) Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 1791. (b) Ruff, J. K. *J. Am. Chem. Soc.* **1965**, *87*, 1140.

(3) Roesky, H. W.; Glemser, O.; Bormann, D. *Chem. Ber.* **1966**, *99*, 1589.

(4) Pankratov, A. V.; Savenkova, N. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1968**, *13*, 1345.

(5) Shamir, J.; Binenboym, J. *J. Mol. Struct.* **1969**, *4*, 100.

(6) Christe, K. O.; Wilson, R. D.; Sawodny, W. *J. Mol. Struct.* **1971**, *8*, 245.

(7) Pulay, P.; Ruoff, A.; Sawodny, W. *Mol. Phys.* **1975**, *30*, 1123.

(8) Mason, J.; Christe, K. O. *Inorg. Chem.* **1983**, *22*, 1849.

(9) Olah, G. A.; Laali, K.; Farnia, M.; Shih, J.; Singh, B. P.; Schack, C. J.; Christe, K. O. *J. Org. Chem.* **1985**, *50*, 1339.

(10) Christe, K. O. *Spectrochim. Acta., Part A* **1986**, *42A*, 939.

(11) Peters, N. J. S. *Chem. Phys. Lett.* **1987**, *142*, 76.

(12) Yakobson, V. V.; Zyubina, T. S.; Charkin, O. P. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1988**, *33*, 1727.

(13) Christe, K. O.; Wilson, R. D.; Wilson, W. W.; Bau, R.; Sukumar, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3795.

(14) Glaser, R.; Choy, G. S. C. *J. Phys. Chem.* **1991**, *95*, 7682.

(15) Christe, K. O.; Dixon, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 2978.

(16) Botschwina, P.; Sebald, P.; Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Mol. Spectrosc.* **1992**, *153*, 255.

(17) As pointed out in ref 16, the NF bond length in the dication NF^{2+}, a species observed by electron impact ionization of NF_3 (Rogers, S. A.; Miller, P. J.; Leone, S. R.; Brehm, B. *Chem. Phys. Lett.* **1990**, *166*, 2971), is computed to be substantially shorter, 1.102 Å (Wang, M. W.; Nobes, R. H.; Bonna, W. J.; Radom, L. *J. Chem. Phys.* **1989**, *891*, 2971). However, this theoretical prediction has not yet been experimentally verified.

(18) See ref 13.

(19) Wilkinson, P. G. *Can. J. Phys.* **1956**, *34*, 250.

(20) (a) For a review on nonaromatic diazonium ions, see: Laali, K.; Olah, G. A. *Rev. Chem. Intermed.* **1985**, *6*, 237. (b) Olah, G. A.; Hegers, R.; Laali, K.; Segal, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 2054.

0020-1669/95/1334-1325$09.00/0

its potentiality as a fluorinating agent, great interest has been devoted to the investigation of its reactivity under various experimental conditions. In liquid HF, F^+ transfer was actually observed from FN_2^+ to Xe and ClF,[13] but the fluorodiazonium ion was found of little practical value for aromatic fluorination.[9]

In conclusion, several details are currently available on the structure and properties of FN_2^+, both in the solid state and in polar fluorinated solvents. By contrast, the experimental evidence concerning gaseous fluorodiazonium ions is scant, being limited to the observation of a FN_2^+ fragment in the mass spectra of *cis-* and *trans-*difluorodiazine.[21] To the best of our knowledge, no structural characterization of isolated FN_2^+ ions has been reported to date, nor is any information available on ionic reactions leading to the formation of gaseous fluorodiazonium ions. The aim of the present paper is to discuss the experimental and theoretical evidence concerning the formation process and the structure of gaseous fluorodiazonium ions obtained from the ionization of a NF_3/HN_3 mixture under typical chemical ionization (CI) conditions.

Experimental Section

Materials. Nitrogen fluoride from Matheson Ltd. and helium from Sol Sud Co. were high-purity research grade gases used without further purification. Vapors of HN_3 were introduced into the ion source of the ZAB-2F and FT-ICR spectrometers by heating ($t \approx 70$ °C) a mixture of sodium azide and stearic acid. ^{15}N-labeled hydrazoic acid was prepared from terminally labeled sodium azide (Cambridge Isotopes Laboratories) having a minimum ^{15}N content of 98 mol %, adopting the same procedure used for unlabeled HN_3.

Mass Spectrometric Measurements. Chemical ionization (CI), mass-analyzed ion kinetic energy (MIKE), and collisionally activated dissociation (CAD) spectra were recorded using a VG Micromass ZAB-2F instrument of magnetic/electrostatic (B/E) configuration.[22] Typical operating conditions of the CI source were as follows: bulk gas pressure 0.1–0.2 Torr; source temperature 180 °C; emission current 1 mA; repeller voltage 0 V; electron energy 100 eV. The relevant ions were focused magnetically into the second field-free region (2nd FFR), and the product ions of the spontaneous fragmentations (MIKE spectra) were detected by varying the deflection voltage of the electrostatic analyzer. The CAD spectra were obtained similarly but by admitting He as a collision gas into the collision cell of the 2nd FFR at such a pressure to reduce the main beam intensity to 70% of its initial value. The MIKE spectra were recorded using an acceleration potential of 8 kV at an energy resolution (fwhm) ranging from 3×10^3 to 4×10^3 and represent the average of at least 40 scans.

The FT-ICR experiments were performed with a Bruker Spectrospin APEX TM 47e spectrometer equipped with an external ion source[23] and a cylindrical "infinity cell",[24] situated between the poles of a superconducting magnet (4.7 T). The measurements were performed as follows. The gaseous mixtures, admitted in the FT-ICR cell at a pressure ranging from 4×10^{-8} to 2×10^{-7} mbar, were ionized by 70 eV electrons. The ions of interest were isolated from all other ions using broad-band and "single-shots" ejection techniques,[25] and their time dependency was obtained by acquiring mass spectra at various reaction times (from 10 ms to 20 s). For the determination of absolute rate constants, the ionization gauge was calibrated on the basis of known reaction rate constants.[26,27] The accuracy of the absolute rate constant measurements is ±25%.

Computational Details. Ab initio quantum-mechanical calculations were performed using a RISC/6000 version of the GAUSSIAN 92 set of programs.[28] The standard internal 6-31G*,[29a] 6-311G**,[29b] 6-311+G**,[29c] and 6-311G**(2df)[29c] basis sets were employed. Geometry optimizations were performed in the full space of the coordinates by analytical gradient-based techniques[30] in the framework of the second-order Møller–Plesset (MP2) theory,[31] employing the 6-31G* basis set. The MP2 theory was used with full electron correlation, including inner-shell electrons. The geometries obtained in this way are denoted as MP2(FULL)/6-31G*. The MP2(FULL)/6-31G* vibrational frequencies were computed for all of the investigated species, in order to characterize them as true minima, transition structures, or higher-order saddle points on the corresponding potential energy hypersurface. The unscaled values obtained were used to calculate the zero-point energies (ZPE's) of the various species. Single-point calculations, at the post-SCF level of theory, were performed within the Møller–Plesset framework up to the fourth order (MP4), by including single, double, triple, and quadruple excitations. A post-MP4 correction for residual correlation energy contributions was accounted for by quadratic configuration interaction, including triple excitations (QCISD(T)). The GAUSSIAN-1 procedure[32,33] was employed to obtain the total energies of the investigated species and the enthalpy change of selected processes.

Mass Spectrometric Results

Preparation of Gaseous FN_2^+ and $F_2HN_2^+$ Ions. Gaseous fluorodiazonium ions, FN_2^+, have been successfully obtained from the ionization of NF_3/HN_3 mixtures in the CI source of the ZAB-2F spectrometer. A typical mass spectrum is shown in Figure 1. Besides the signals arising from the ionization of NF_3 and HN_3, two additional peaks are detected, the more intense one at $m/z = 47$ and the less intense but well-detectable one at $m/z = 67$, attributable to the formation of a $F_2HN_2^+$ ion. Confirmatory tests have been performed using terminally labeled hydrazoic acid, consisting of an equimolar mixture of $H-^{15}N-N_2$ and $HNN-^{15}N$. Under these conditions, two pairs of equally intense peaks are detected, at $m/z = 47$ and 48 and at $m/z = 67$ and 68, respectively. These findings are significant, in that they demonstrate the incorporation of at least one of the terminal nitrogen atoms of HN_3 in both FN_2^+ and $F_2HN_2^+$.

Collisionally Activated Dissociation and Mass-Analyzed Ion Kinetic Energy Experiments. Positive evidence for the assignment of the signals at $m/z = 47$ and 67 in the CI spectrum of the NF_3/HN_3 mixture to FN_2^+ and $F_2HN_2^+$ has been obtained by structurally diagnostic[34] mass spectrometric techniques. Collisionally activated dissociation[35] (CAD) and mass-analyzed

---

(21) Klopotek, D. L.; Hobrock, B. G. *Inorg. Chem.* **1967**, *6*, 1750 and references therein.

(22) Morgan, R. P.; Beynon, J. H.; Bateman, R. H.; Green, B. N. *Int. J. Mass Spectrom. Ion Processes* **1978**, *28*, 171.

(23) Kofel, P.; Allemann, M.; Kellerhals, H. P.; Wanczek, K. P. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 97.

(24) Caravatti, P.; Allemann, M. *Org. Mass Spectrom.* **1991**, *26*, 514.

(25) de Koning, L. J.; Fokkens, R. H.; Pinkse, F. A.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1987**, *77*, 95.

(26) Lin, Y.; Ridge, D. P.; Munson, B. *Org. Mass Spectrom.* **1991**, *26*, 550.

(27) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.

(28) Frish, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Ragavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992.

(29) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. (b) Krishnann, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *Ibid.* **1980**, *72*, 4244. (c) Frish, M. J.; Pople, J. A.; Binkley, J. S. *Ibid.* **1984**, *80*, 3265.

(30) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(31) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 86.

(32) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Ragavachari, R.; Curtis, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.

(33) (a) Radom, L. *Org. Mass Spectrom.* **1991**, *266*, 359. (b) Ma, N. L.; Smith, B. J.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1991**, *113*, 7903. (c) Durant, R.; Rohlfing, C. *J. Chem. Phys.* **1993**, *98*, 8031.

(34) The term "structure" is used to denote the "connectivity" of a species rather than its detailed geometry (bond lengths, bond angles, dihedral angles).

(35) Reviews: (a) Levsen, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 609. (b) Cooks, R. G., Ed. *Collision Spectroscopy*; Plenum: New York, 1978. (c) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1985**, *3*, 77. (d) Bordas-Nagy, J.; Jennings, K. R. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 105.

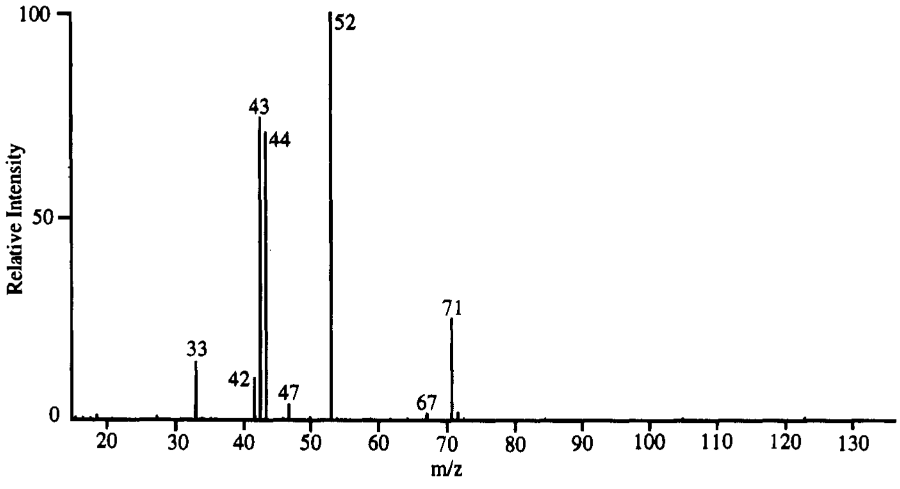

Figure 1. Mass spectrum of a NF_3/HN_3 gaseous mixture (2/1; $p \approx 0.1$ mbar) introduced into the CI source of the ZAB-2F spectrometer.

Table 1. CAD Spectral Data for FN_2^+, $FN^{15}N^+$, and $F_2HN_2^+$

	relative intensities[a]		
m/z	FN_2^+	$FN^{15}N^+$	$F_2HN_2^{+\,b}$
52			27.9
34		6.0	
33	38.7	35.5	12.8
29		47.7	51.0
28	54.2		
20			3.1
19	1.5	1.3	
15		4.4	2.6
14	5.6	5.1	2.6

[a] The intensities are normalized with respect to the sum of the intensities. [b] The peak at $m/z = 47$ has been excluded because of the unimolecular contribution to its formation (see text).

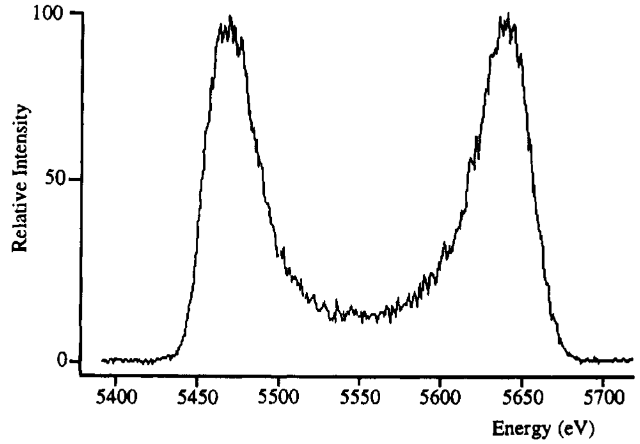

Figure 2. MIKE peak for the decomposition $F_2N{-}NH^+ \rightarrow FN_2^+ + HF$.

ion kinetic energy[36] (MIKE) spectrometry have been used to probe the fragmentation patterns, reported in Table 1, and the unimolecular decomposition processes of these two ions.

The nature of the fragments in the CAD spectrum of the ions at $m/z = 67$ confirms the $F_2HN_2^+$ elemental composition and, in addition, provides information on their connectivity. In fact, from Table 1, an intense NF_2^+ fragment at $m/z = 52$ is detected, which accounts for 28% of the total intensity. This finding is structurally informative, in that the F atoms appear to be bound to the same N atom, thus pointing to a $F_2N{-}NH^+$ connectivity. On the other hand, on the basis of the detection of a minor $HF^{\bullet+}$ fragment, at $m/z = 20$, there is evidence for the formation of ions of $FN_2{-}FH^+$ structure. The mixed character of the $F_2HN_2^+$ ionic population is not inconsistent with the nature of the other fragments. In fact, whereas the intense N_2H^+ ion, at $m/z = 29$, and the less intense $NH^{\bullet+}$, at $m/z = 15$, can arise from the fragmentation of $F_2N{-}NH^+$ ions, the signal at $m/z = 33$, corresponding to $NF^{\bullet+}$, can be equally well attributed to $F_2N{-}NH^+$ and $FN_2{-}FH^+$ isomers. In addition, due to the ion–dipole character of the $FN_2{-}FH^+$ ions (*vide infra*), a substantial contribution of the FN_2^+ fragment is expected in the corresponding CAD spectrum, an expectation fully verified. However, as outlined below, the loss of HF is also observed in the MIKE spectrum of $F_2HN_2^+$. Thus, in Table 1, the FN_2^+ fragment was not included in the CAD fragmentation pattern, and the reported relative abundances have been calculated on the basis of the sum of all the remaining ions. The nature of the fragments in the MIKE spectrum of the $F_2HN_2^+$ ions, showing the loss of HF as the only unimolecular decomposition, does not help in the assignment of their connectivity. However, the shape of the MIKE peak, reproduced in Figure 2, and the corresponding kinetic energy release (KER), as large as 1.6 eV at the half-height of the peak ($T_{0.5}$), are particularly telling. In fact, large kinetic releases and dish-topped peaks are generally indicative[36,37] of high reverse activation energies, typical of those fragmentation processes, like HF elimination from ions of $F_2N{-}NH^+$ connectivity, that require prior rearrangement of the decomposing ions. On the other hand, dissociations involving direct bond cleavage, like the loss of HF from $FN_2{-}FH^+$ ions, have little or no reverse activation energies and generally give rise to narrow (Gaussian-type) peaks.[36,37]

The CAD spectrum of the ions at $m/z = 47$ (see Table 1), showing the two intense signals at $m/z = 28$, $N_2^{\bullet+}$, and $m/z = 33$, $NF^{\bullet+}$, which account for more than 90% of the whole ionic pattern, and the less intense ones at $m/z = 14$, N^+, and $m/z = 19$, F^+, allows unambiguous assignment to a FN_2^+ ion. Moreover, the comparison with the CAD spectrum of the ion at $m/z = 48$ obtained from the ionization of a mixture of nitrogen fluoride and labeled hydrazoic acid, is highly informative from the structural standpoint. In fact, from Table 1, the detection in the CAD spectrum of the ^{15}N-labeled ion of an intense $NF^{\bullet+}$ fragment at $m/z = 33$ and of a significantly less intense peak at $m/z = 34$, $^{15}NF^+$ (observed ratio ≈ 6), clearly demonstrates that *the two nitrogen atoms of the FN_2^+ ion are not structurally equivalent*. In addition, it can be concluded that the fluorine

---

(36) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.

(37) (a) Holmes, J. L.; Terlow, J. K. *Org. Mass Spectrom.* **1980**, *15*, 393. (b) Holmes, J. L. *Ibid.* **1985**, *20*, 1669. (c) Bowen, R. D.; Williams, D. H.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 451.

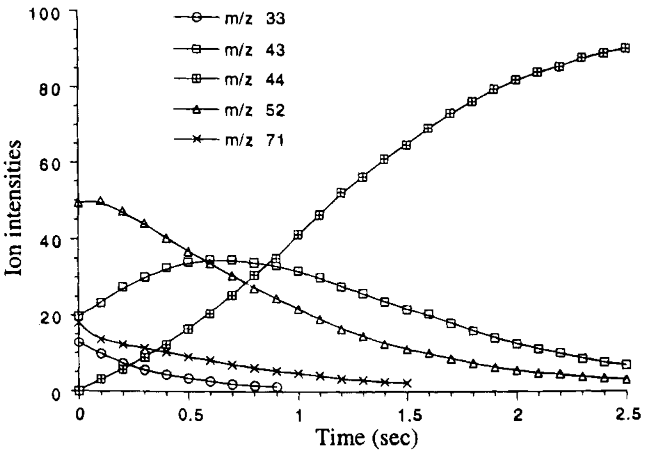

Figure 3. Time dependence of ion abundances following ionization of a NF_3 ($p = 1.1 \times 10^{-7}$ mbar) and HN_3 ($p = 4.5 \times 10^{-8}$ mbar) mixture.

atom of the asymmetric $FN^{15}N^+$ ion is preferentially bound to the ^{14}N atom. From Table 1, the peak at $m/z = 28$, $N_2^{\bullet+}$, detected in the CAD spectrum of FN_2^+, shifts to $m/z = 29$, $^{15}NN^{\bullet+}$, in the CAD spectrum of $FN^{15}N^+$, thus confirming the existence of a direct nitrogen–nitrogen bond in both ions. Finally, the FN_2^+ ions do not undergo any observable metastable decomposition, giving blank MIKE spectra.

In conclusion, it appears that the structurally diagnostic mass spectrometric techniques employed and the labeling experiments performed indicate the formation, from an ionized NF_3/HN_3 mixture, of an asymmetric FN_2^+ ion, which incorporates at least one of the terminal nitrogen atoms of HN_3. This ion originates from the unimolecular loss of HF from a $F_2HN_2^+$ moiety, detected as well in the CI plasma. The strong kinetic energy release associated with this decomposition indicates that its reverse reaction

$$FN_2^+ + HF \rightarrow F_2HN_2^+ \qquad (1)$$

is characterized by a substantial activation barrier.[36]

Fourier-Transform Ion Cyclotron Resonance Experiments. The FN_2^+ and $F_2HN_2^+$ ions, not observed in the mass spectra of pure NF_3 and HN_3, clearly arise from the ion–molecule reaction(s) promoted by the ionization of the NF_3/HN_3 mixtures. These ionic processes can be usefully investigated by Fourier-transform ion cyclotron resonance[38] (FT-ICR) spectrometry.

Irrespective of the NF_3:HN_3 stoichiometry, which has been changed from ca. 5:1 to ca. 1:1, four ions of appreciable intensity are obtained by electron impact (70 eV) ionization of a mixture of NF_3 and HN_3 introduced into the resonance cell of the FT-ICR spectrometer, *i.e.* $NF^{\bullet+}$, $m/z = 33$, NF_2^+, $m/z = 52$, $NF_3^{\bullet+}$, $m/z = 71$, and $HN_3^{\bullet+}$, $m/z = 43$. A representative plot of the ionic abundances vs the reaction time is shown in Figure 3. The salient feature is that no signals are detected at $m/z = 47$ and $m/z = 67$, suggestive of the formation of FN_2^+ and $F_2HN_2^+$ ions, on increasing the reaction time. Rather, in the low-pressure domain typical of the ICR cell, the gas-phase ion chemistry of the NF_3/HN_3 mixtures is dominated by the formation of protonated hydrazoic acid, $H_2N_3^+$, at $m/z = 44$, whose intensity monotonically increases with the reaction time. Moreover, from Figure 3, the $NF_3^{\bullet+}$, NF_2^+, and $NF^{\bullet+}$ signals monotonically decrease, vanishing at long reaction times, whereas the $HN_3^{\bullet+}$ signal monotonically decreases after reaching a maximum. These observations allow a simple interpretation of the reaction sequence promoted by ionization of the NF_3/HN_3 mixtures at low pressure. The intermediate $HN_3^{\bullet+}$ radical cations, generated by the electron transfer reactions

$$NF_3^{\bullet+} + HN_3 \rightarrow NF_3 + HN_3^{\bullet+} \qquad (2)$$

$$NF_2^+ + HN_3 \rightarrow NF_2^{\bullet} + HN_3^{\bullet+} \qquad (3)$$

$$NF^{\bullet+} + HN_3 \rightarrow NF^{\bullet} + HN_3^{\bullet+} \qquad (4)$$

are unreactive toward NF_3, undergoing instead H atom abstraction from HN_3, giving protonated hydrazoic acid:

$$HN_3^{\bullet+} + HN_3 \rightarrow H_2N_3^+ + N + N_2 \qquad (5)$$

As a matter of fact, the exothermic reaction (5), $\Delta H_5° = -78.7$ kJ mol^{-1},[39,40] has been so far successfully employed for the preparation of gaseous $H_2N_3^+$ ions under CI conditions.[41] From the enthalpies of formation of the species involved, the following enthalpy changes can be calculated: $\Delta H_2° = -216.7$ kJ mol^{-1}, $\Delta H_3° = -82.8$ kJ mol^{-1}, and $\Delta H_4° = -147.7$ kJ mol^{-1}.

The above interpretation of the ionic time dependencies reported in Figure 3 has been confirmed by independent experiments involving $NF_3^{\bullet+}$, NF_2^+, $NF^{\bullet+}$, and $HN_3^{\bullet+}$ ions, isolated by selective-ejection techniques and allowed to react with the gaseous NF_3/HN_3 mixture. A representative plot of the time dependence of the abundances of all the ionic species formed from the $NF_3^{\bullet+}$ radical cation is shown in Figure 4a. The intensity of the $NF_3^{\bullet+}$ signal exponentially decreases to form the $HN_3^{\bullet+}$ radical, which in turn gives the $H_2N_3^+$ ion. From the average of different independent runs, the rate constant of reaction 2 is evaluated as $k_2 = (1.2 \pm 0.3) \times 10^{-9}$ cm^3/(molecule s). From the corresponding collision rate constant, calculated according to the average dipole orientation theory[42] as k_2(ADO) $= 1.05 \times 10^{-9}$ cm^3/(molecule s), the efficiency of reaction 2, k_2/k_2(ADO), is obtained as high as 1.1 ± 0.3, as expected for an exothermic electron transfer process. From Figure 4a, a small but well detectable formation of NF_2^+ is observed, due to the unimolecular decomposition of excited $NF_3^{\bullet+}$ ions. Together with the fluoride ion abstraction by $NF^{\bullet+}$ from NF_3 (*vide infra*), this process is responsible of the slight increase of the relative intensity of the NF_2^+ signal observed in Figure 3 at short reaction times.

The time dependence of the abundances of the ionic species formed from the isolated NF_2^+ ion, shown in Figure 4b, closely resembles that from the isolated $NF_3^{\bullet+}$ radical cation. Only electron transfer (3) is observed, the rate constant of which is evaluated as $k_3 = (1.2 \pm 0.3) \times 10^{-9}$ cm^3/(molecule s) from the exponential decrease of the relative intensity of NF_2^+. From the calculation of k_3(ADO), 1.12×10^{-9} cm^3/(molecule s), the efficiency of reaction 3, k_3/k_3(ADO), is obtained as 1.1 ± 0.3.

Besides the electron transfer reaction (4), the fluoride ion

---

(38) (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 28. (b) *Can. J. Chem.* **1974**, *52*, 1997. (c) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316.

(39) Unless stated otherwise, thermochemical data are taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(40) The enthalpy of formation of $H_2N_3^+$, 1071.1 kJ mol^{-1}, has been derived from the recent estimate of the proton affinity of HN_3, 753.1 kJ mol^{-1} (Cacace, F.; Attinà, M.; Speranza, M.; de Petris, G.; Grandinetti, F. *J. Org. Chem.* **1993**, *58*, 3639).

(41) Cacace, F.; Attinà, M.; de Petris, G.; Grandinetti, F.; Speranza, M. *Gazz. Chim. Ital.* **1990**, *120*, 691.

(42) (a) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347. (b) *Ibid.* **1975**, *17*, 211.

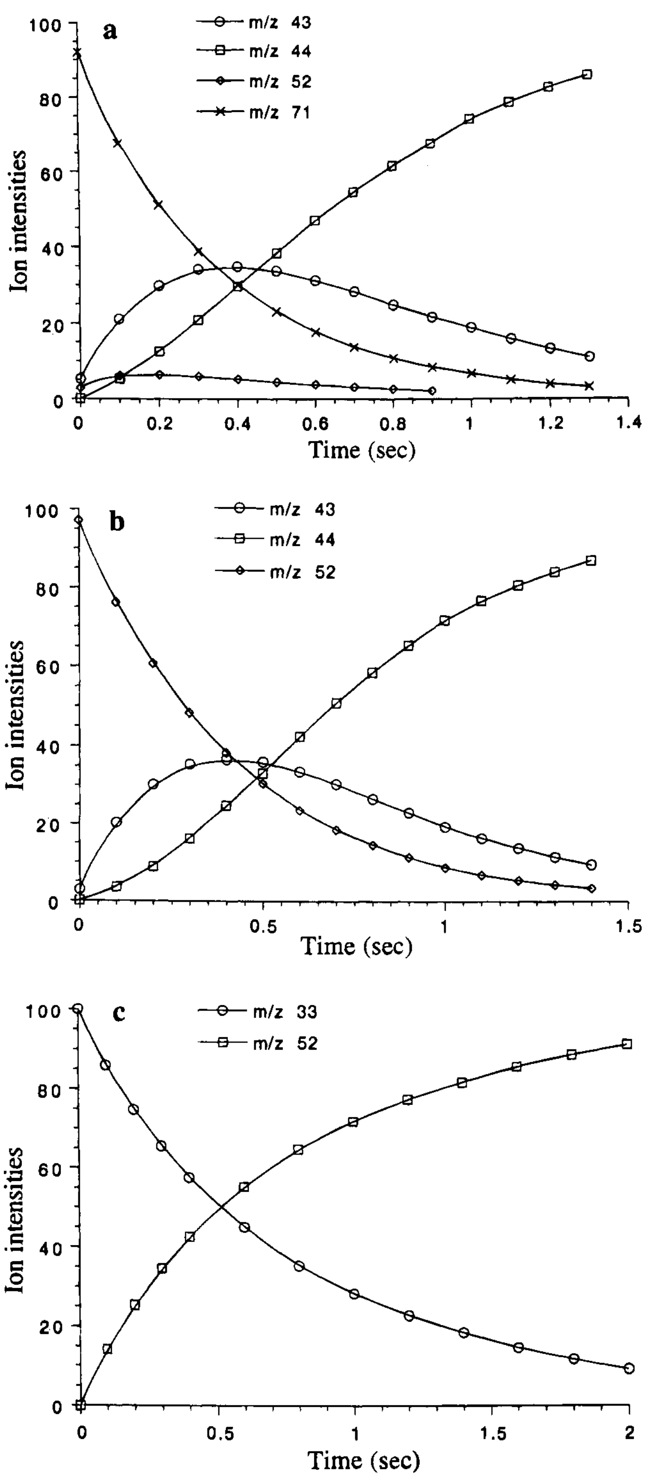

Figure 4. (a) Time dependence of ion abundances following ionization of a NF_3 ($p = 9.6 \times 10^{-8}$ mbar) and HN_3 ($p = 9.2 \times 10^{-8}$ mbar) mixture and isolation of $NF_3^{\bullet+}$. (b) Time dependence of ion abundances following ionization of a NF_3 ($p = 9.6 \times 10^{-8}$ mbar) and HN_3 ($p = 9.2 \times 10^{-8}$ mbar) mixture and isolation of NF_2^+. (c) Time dependence of ion abundances following ionization of NF_3 ($p = 1.4 \times 10^{-7}$ mbar) and isolation of $NF^{\bullet+}$.

abstraction reaction

$$NF^{\bullet+} + NF_3 \rightarrow NF_2^+ + NF_2^\bullet \qquad (6)$$

is responsible for the exponential decrease of $NF^{\bullet+}$ in Figure 3. The occurrence of the exothermic reaction (6), $\Delta H_6° = -100.4$ kJ mol^{-1}, has been confirmed by independent experiments involving isolated $NF^{\bullet+}$ ions in the presence of NF_3 alone. As a matter of fact, the fluoride ion abstraction (6) represents the only appreciable ion−molecule reaction following the ionization of pure NF_3. The corresponding time dependence of the ionic abundances is shown in Figure 4c. The $NF^{\bullet+}$ signal exponentially decreases with a rate constant of $(3.6 \pm 0.9) \times 10^{-10}$ cm^3/(molecule s). From the collision rate constant k_6(ADO) = 8.0×10^{-10} cm^3/(molecule s), the efficiency of this process is evaluated as 0.45 ± 0.1. From Figure 3, taking into account the contribution of reaction 6 to the overall decrease of the $NF^{\bullet+}$ signal, the rate constant of the electron transfer reaction (4) can be evaluated as $(1.45 \pm 0.4) \times 10^{-9}$ cm^3/(molecule s), with an efficiency of 1.15 ± 0.3, derived from the calculation of k_4(ADO), 1.26×10^{-9} cm^3/(molecule s). Finally, independent isolation experiments confirmed that in the NF_3/HN_3 mixtures the $HN_3^{\bullet+}$ radical cation undergoes hydrogen atom abstraction from HN_3 as the only observable ion−molecule reaction. The formed $H_2N_3^+$ ions, whose abundance has been monitored up to several tens of seconds, are in turn unreactive in the same gaseous mixtures.

In conclusion, the FT-ICR experiments indicate that, under the low-pressure domain of the ICR cell, the gas-phase ion chemistry of the NF_3/HN_3 mixtures essentially consists of the fast electron transfer reactions (2)−(4) from the neutral HN_3 to the $NF_3^{\bullet+}$, NF_2^+, and $NF^{\bullet+}$ ions. The $HN_3^{\bullet+}$ radical cation is in turn able to undergo hydrogen atom abstraction from HN_3, and the so formed $H_2N_3^+$ ions, unreactive in the NF_3/HN_3 mixtures, are by far the dominating species at long reaction times.

Theoretical Results

Whereas no experimental information is available on the structure and the stability of the various $F_2HN_2^+$ isomers, nor on the thermochemistry of FN_2^+, the investigation of these aspects is well within the capabilities of routinely available theoretical methods,[43] and several calculations concerning various FN_2^+ isomers and their interconnecting transition structures have been reported.[7,10−12,14−16] On the other hand, no theoretical data are available on the $F_2HN_2^+$ ions. Thus, ab initio calculations, up to the GAUSSIAN-1 level of theory, have been performed to get the necessary information for the discussion of the mass spectrometric experiments.

At the MP2(FULL)/6-31G* level of theory, four distinct minima have been identified on the $F_2HN_2^+$ potential energy surface, i.e. the $F_2N{-}NH^+$ ion, **1**, the *cis*- and *trans*-$FNH{-}NF^+$ ions, **2** and **3**, and the ion−dipole complex $FN_2{-}FH^+$, **4**. The corresponding optimized geometries are shown in Figure 5, the total energies, at the various computational levels are collected in Table 2, and the corrections for the evaluation of the GAUSSIAN-1 energies are listed in Table 3. From Figure 5, the computed N−N, N−F, and N−H bond distances of ions **1**−**3** indicate the formation of covalently bound species, whereas the ion−dipole character of ion **4** clearly emerges from the large distance between the FN_2^+ and HF fragments. From Table 3, the corresponding interaction energy is derived as 51.9 kJ mol^{-1} at the GAUSSIAN-1 level of theory. At the same computational level, ion **4** is by far the most stable among the investigated $F_2HN_2^+$ isomers. The computed energy difference with *cis*-$FNH{-}NF^+$ is as large as 127.6 kJ mol^{-1}, and the latter species is in turn more stable than the trans isomer by 13.4 kJ mol^{-1}. Ion **1** is the less stable among the investigated isomers, an energy difference of 151.0 kJ mol^{-1} being computed with respect to ion **4**. From the GAUSSIAN-1 energies of Table 3, corrected for the thermal contributions at 300 K, the enthalpy change of

---

(43) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

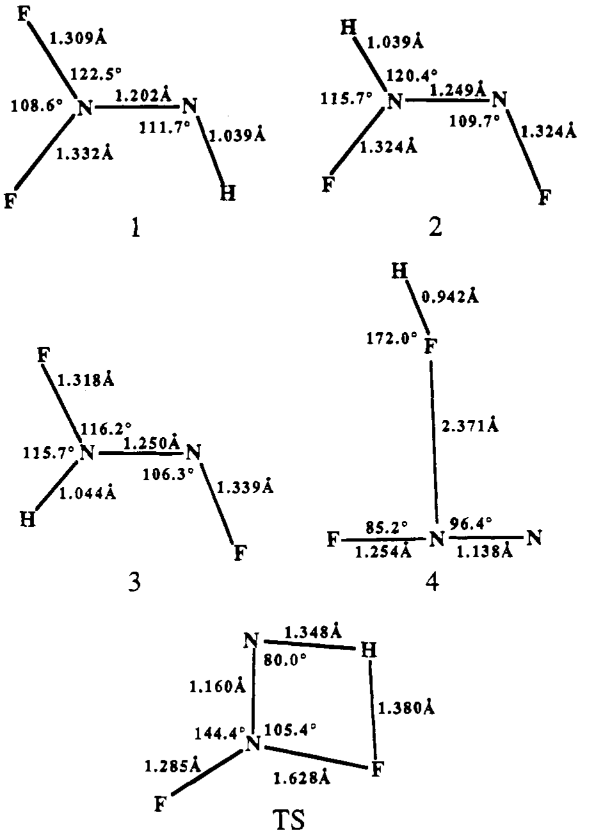

Figure 5. MP2(FULL)/6-31G*-optimized geometries of the investigated $F_2HN_2^+$ ions.

the process

$$NF_2^+ + HN_3 \rightarrow FN_2{-}FH^+ + N_2 \tag{7}$$

is computed as $\Delta H_7°$(300 K) = −559.8 kJ mol^{-1}, which, combined with the experimental enthalpies of formation of NF_2^+, 1150.6 kJ mol^{-1}, HN_3, 294.1 kJ mol^{-1}, and N_2, leads to an enthalpy of formation of 884.9 kJ mol^{-1} for the $FN_2{-}FH^+$ ion **4**. From the above energy differences among the various $F_2HN_2^+$ isomers, the heats of formation of ions **1**−**3** are obtained as 1036.0, 1012.5, and 1025.9 kJ mol^{-1}, respectively.

The mechanism of the HF elimination from **1** has been also investigated. The results indicate a two-step process, which involves prior isomerization of **1** into **4**. This hydrogen migration process occurs through the four-center transition structure **TS**, the MP2(FULL)/6-31G* optimized geometry of which is shown in Figure 5. This ion possesses a single imaginary frequency of −2313.3 cm^{-1}, associated with the in-plane motion of the hydrogen atom from nitrogen to fluorine. From the energy difference between **TS** and **1**, the energy barrier of the isomerization process is computed to be as large as 219.2 kJ mol^{-1} at the GAUSSIAN-1 level of theory.

The formation of the FN_2^+ and $F_2HN_2^+$ ions in the CI experiments can reasonably involve the intermediacy of a NF_2^+/HN_3 adduct (*vide infra*). In this connection, the experimentally unknown structure and stability of ions **5** and **6** arising from

$$\underset{\mathbf{5}}{F_2N{-}NH{-}N_2^+} \qquad \underset{\mathbf{6}}{HN{-}N_2{-}NF_2^+}$$

the addition of NF_2^+ to the terminal nitrogen atoms of HN_3 have been theoretically investigated. The geometries of these species have been optimized at the MP2(FULL)/6-31G* level of theory, and single-point calculations have been performed at the MP4(SDTQ)/6-311G** level. The obtained total energies are listed in Table 2. From their vibrational frequencies, both of these two ions correspond to absolute minima on the potential energy surface. However, whereas the attachment of NF_2^+ to the nitrogen atom of the HN− group of HN_3 leads to the covalently-bound species **5**, characterized by a $F_2N{-}NH$ bond length of 1.392 Å, the distance between the NF_2^+ and HN_3 groups in ion **6** is as large as 1.902 Å. Consistently, from Table 2, at the MP4(SDTQ)/6-311G**//MP2(FULL)/6-31G* + ZPE-(MP2(FULL)/6-31G*) level of theory, the binding energies of **5** and **6** with respect to the separate NF_2^+ and HN_3 fragments are quite different and amount to 213.0 and 136.8 kJ mol^{-1}, respectively. It is interesting to point out that the MP2(FULL)/6-31G* energy difference between isomers **5** and **6**, 101.2 kJ mol^{-1}, matches the available results concerning protonated HN_3.[41] In fact, MP2/6-31G* ab initio calculations revealed that the aminodiazonium ion $H_2N{-}N_2^+$ is more stable than the iminodiazenium ion $HN{=}N{=}NH^+$ by 101.2 kJ mol^{-1}.[41]

Finally, from Table 3, the enthalpy change of the process

$$NF_2^+ + HN_3 \rightarrow FN_2^+ + HF + N_2 \tag{8}$$

is evaluated as $\Delta H_8°$(300 K) = −502.9 kJ mol^{-1} at the GAUSSIAN-1 level of theory. Combining this theoretical enthalpy change with the experimental enthalpies of formation of NF_2^+, HN_3, N_2, and HF, −272.4 kJ mol^{-1}, a *theoretical* value of 1214.2 kJ mol^{-1} is obtained for the experimentally unknown enthalpy of formation of the fluorodiazonium ion. This finding is not inconsistent with a recent theoretical estimate of 1182.8 kJ mol^{-1}, based on local density functional calculations,[15] but significantly lower than a previous estimate of 1376.5 kJ mol^{-1}.[11]

Discussion

The mass spectrometric and theoretical results outlined in the previous sections support the reaction sequence

$$NF_2^+ + HN_3 \rightarrow NF_2^{\bullet} + HN_3^{\bullet+} \tag{9a}$$

$$NF_2^{\bullet} + HN_3^{\bullet+} \rightarrow [F_2N{-}NH{-}N_2^+]_{exc} \tag{9b}$$

$$[F_2N{-}NH{-}N_2^+]_{exc} \rightarrow F_2N{-}NH^+ + N_2 \tag{9c}$$

$$F_2N{-}NH^+ \rightarrow FN_2^+ + HF \tag{9d}$$

as a plausible route to gaseous $F_2HN_2^+$ and FN_2^+ cations from the ionization of a NF_3/HN_3 mixture under CI conditions.

The highly-efficient electron transfer reaction (9a), actually observed by FT-ICR spectrometry, can be reasonably assumed as the first link of the overall sequence. The fate of the initially formed $NF_2^{\bullet}$ and $HN_3^{\bullet+}$ radicals strictly depends on the experimental conditions. In the low-pressure domain of the ICR cell ($P \approx 10^{-7}$ mbar), the conceivable condensation product cannot be stabilized by unreactive collisions. Rather, the two fragments simply fly apart, and $HN_3^{\bullet+}$ is the only ion detected. By contrast, in the higher-pressure range of the CI source ($P \approx$ 0.1 mbar), the ion−molecule electrostatic complex formed by the $NF_2^{\bullet}$ and $HN_3^{\bullet+}$ fragments is partially stabilized by collisions with the buffer gas. Reaction 9b, predicted by the post-SCF ab initio calculations, occurs in the complex, leading to formation of the $F_2N{-}NH{-}N_2^+$ ion **5**. In fact, at the MP4-(SDTQ)/6-311G**//MP2(FULL)/6-31G* + ZPE(MP2(FULL)/6-31G* level of theory, this isomer is found to be more stable than the alternative conceivable adduct $HN{-}N_2{-}NF_2^+$ by 76.1

Table 2. Absolute Energies (hartrees) of the Investigated $F_2HN_2^+$ and $F_2HN_4^+$ Ions and Their Fragments

	MP2(FULL)/6-31G*				
species	MP2(FULL)/6-31G*	MP4/6-311G**	MP4/6-311+G**	MP4/6-311G**(2df)	QCISD(T)/6-311G**
F_2N-NH^+, **1**	−308.48516	−308.68765	−308.69829	−308.84851	−308.68479
cis-$FNH-NF^+$, **2**	−308.49674	−308.69914	−308.71065	−308.85809	−308.69468
trans-$FNH-NF^+$, **3**	−308.49118	−308.69354	−308.70485	−308.85227	−308.68942
FN_2-FH^+, **4**	−308.54304	−308.75189	−308.76690	−308.90212	−308.74290
TS	−308.39686	−308.60155	−308.61320	−308.76217	−308.59378
$F_2N-NH-N_2^+$, **5**	−417.68976	−417.94128			
$F_2N-N_2-NH^+$, **6**	−417.64925	−417.91043			
FN_2^+	−208.33359	−208.45586	−208.46046	−208.55969	−208.44722
NF_2^+	−253.24027	−253.41074	−253.41847	−253.53831	−253.40292
HN_3	−164.35125	−164.44608	−164.45353	−164.53491	−164.43420
N_2	−109.26157	−109.31616	−109.32092	−109.36984	−109.31022
HF	−100.18416	−100.27373	−100.28582	−100.31962	−100.27345

Table 3. MP4/6-311G** Absolute Eneriges (hartrees) and Corrections (millihartrees) for the Evaluation of the GAUSSIAN-1 Energies of the $F_2HN_2^+$ Ions and Their Fragments

species	MP4/6-311G**	$\Delta E(+)$	$\Delta E(2df)$	$\Delta E(QCI)$	$\Delta E(HLC)$	$\Delta E(ZPE)$	Gaussian-1
F_2N-NH^+, **1**	−308.68765	−10.64	−160.86	+2.86	−73.68	25.52	−308.90445
cis-$FNH-NF^+$, **2**	−308.69914	−11.51	−158.95	+4.46	−73.68	25.46	−308.91336
trans-$FNH-NF^+$, **3**	−308.69354	−11.31	−158.73	+4.12	−73.68	24.84	−308.90830
FN_2-FH^+, **4**	−308.75189	−15.01	−150.23	+8.99	−73.68	19.90	−308.96192
TS	−308.60155	−11.65	−160.62	+7.77	−73.68	18.75	−308.82098
FN_2^+	−208.45586	−4.6	−103.83	+8.64	−49.12	9.33	−208.59544
NF_2^+	−253.41074	−7.73	−127.57	+7.82	−55.26	7.92	−253.58556
HN_3	−164.44608	−7.45	−88.83	+11.88	−49.12	21.52	−164.55808
N_2	−109.31616	−4.76	−53.68	+5.94	−30.7	4.94	−109.39442
HF	−100.27373	−12.09	−45.89	+0.28	−24.56	9.20	−100.34679

kJ mol^{-1}. Moreover, at the same computational level, the dissociation of **5** into F_2N-NH^+ and N_2 is predicted to be exothermic by 170.3 kJ mol^{-1}. Thus, it is reasonable to assume that the energy barrier associated with the dissociation of **5** (reaction 9c) is significantly lower than the exothermicity of its formation process (9a) and (9b) computed as 213.0 kJ mol^{-1}. Under this assumption, the $F_2N-NH-N_2^+$ ions, formed in a high degree of vibrational excitation, cannot be trapped in a potential well deep enough to allow their observation in the CI experiments. Rather, they undergo fast unimolecular loss of N_2, giving the $F_2HN_2^+$ ions eventually observed in the CI plasma. In keeping with reaction sequence (9a)−(9c) the CAD experiments support the formation of ions of F_2N-NH^+ connectivity. In addition, the incorporation of the nitrogen atom of the HN− group of HN_3 in the $F_2HN_2^+$ ions is predicted. This explains the detection of the two equally intense signals due to the F_2N-NH^+ ion at $m/z = 67$ and to the $F_2N-{}^{15}NH^+$ ion at $m/z = 68$ in the CI experiments performed using terminally labeled hydrazoic acid.

The observation of gaseous F_2N-NH^+ ions provides the first experimental evidence for the existence of stable isolated F_2N-NX^+ ions, whose formation in the solid state[44] (X = F) has been regarded with considerable interest, since they could represent potential precursors of nitrenium ions.[45] In particular, the solid adduct obtained from the reaction

$$N_2F_4 + SbF_5 \rightarrow N_2F_3^+SbF_6^-$$

has been identified and structurally characterized by vibrational and ^{19}F NMR spectroscopy.[46] Consistent with the present theoretical results which identify the fully-planar F_2N-NH^+ ion as a stable minimum on the potential energy surface, all the experimental data pointed to a F_2N-NF^+ planar structure of C_s symmetry for the $N_2F_3^+$ ions.

The $F_2HN_2^+$ ions undergo HF loss as the only observed metastable decomposition, thus providing evidence for reaction 9d. Assuming formation of F_2N-NH^+ ions, the results of the ab initio GAUSSIAN-1 calculations, combined with the evidence from the MIKE experiments, allow a detailed discussion of the mechanism of this process. The obtained potential energy profile is schematized in Figure 6. At the GAUSSIAN-1 level of theory, the addition−elimination sequence (9a)−(9c) is predicted to be exothermic by 407.5 kJ mol^{-1}. Thus, some F_2N-NH^+ ions can be formed with excess internal energy sufficient to overcome the barrier imposed by the transition structure **TS**, 219.2 kJ mol^{-1}, isomerizing to FN_2-FH^+ and eventually dissociating into FN_2^+ and HF. If this process occurs in the metastable time window ($10^{-5}-10^{-4}$ s), the large energy difference between **TS** and the dissociation products, computed as 333.0 kJ mol^{-1} at the GAUSSIAN-1 level of theory, leads to the large KER denoted by the dish-topped peak shown in Figure 2. In keeping with the structural features of FN_2^+ and HF, the corresponding $T_{0.5}$, 1.6 eV, which accounts for ca. 50% of the above energy difference, indicates a partition of the energy released that favors the translational over the rotational and/or internal degrees of freedom of the fragments. The F_2N-NH^+ ions can also undergo isomerization already in the ion source. The obtained FN_2-FH^+ ions, thermalized by unreactive collisions, can be sampled by CAD spectrometry, whose results support the existence of a structurally mixed $F_2HN_2^+$ population.

The fluorodiazonium ions FN_2^+, abundantly formed in the CI experiments, are obtained via the reaction sequence (9a)−(9d). All the ab initio calculations reported to date on this species[7,10−12,14−16] identify the asymmetric, linear $F-N-N^+$ ion as the global minimum on the FN_2^+ potential energy surface, the alternative conceivable cyclic isomer of C_{2v} symmetry being less stable by ca. 273.6 kJ mol^{-1}.[14] In keeping with previous structural studies in the solid state,[1−6,13] in polar fluorinated solvents,[8] and in a nitrogen-cooled discharge,[16] the results of the present mass spectrometric study are fully consistent with

---

(44) (a) Ruff, J. K. *J. Am. Chem. Soc.* **1965**, *87*, 1140. (b) Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 1791. (c) Young, A. R.; Moy, D. *Inorg. Chem.* **1967**, *6*, 178. (d) Lawless, E. W. *Anal. Lett.* **1967**, *1*, 153. (e) Qureshi, A. M.; Aubke, A. F. *Can. J. Chem.* **1970**, *48*, 3117.

(45) Olah, G. A.; Prakash, G. K. S.; Sommer, J.; *Superacids*; Wiley: New York, 1985.

(46) Christe, K. O.; Schack, C. J. *Inorg. Chem.* **1978**, *17*, 2749.

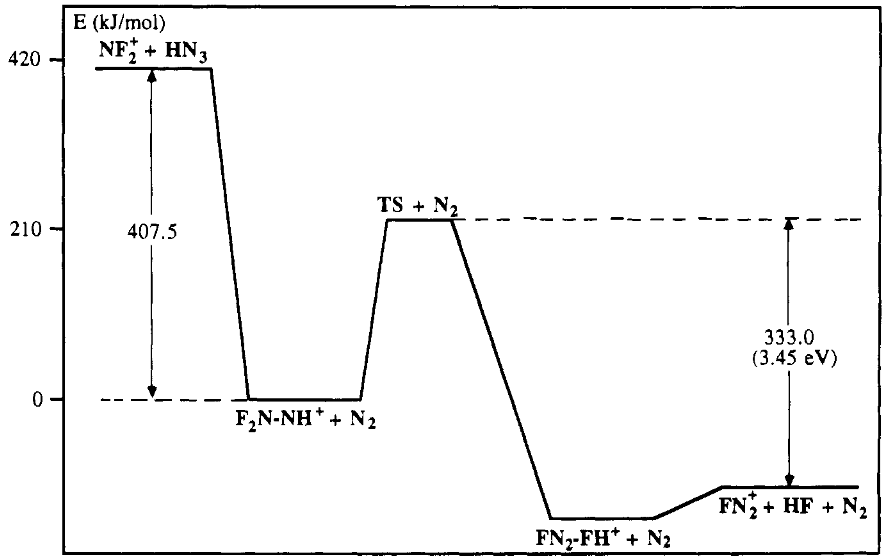

Figure 6. GAUSSIAN-1 potential energy diagram for the reaction $NF_2^+ + HN_3 \rightarrow FN_2^+ + HF + N_2$.

this theoretical prediction. In fact, the CAD experiments performed on the ^{15}N-labeled ions $FN^{15}N^+$, obtained from the ionization of mixtures of nitrogen fluoride and terminally labeled hydrazoic acid, clearly demonstrate that the two nitrogen atoms of FN_2^+ are not structurally equivalent. In addition, the observation of a major FN^+ fragment and a significantly minor $F^{15}N^+$ one, together with the indication from the ab initio calculations, allow us to conclude that the linear $F-N-{}^{15}N^+$ ions are obtained from the labeling experiments. This specification of the nitrogen atoms is also consistent with the mechanism of formation of the $FN^{15}N^+$ ions, expected to arise from the unimolecular HF loss from $F_2N-{}^{15}NH^+$. Furthermore, the observation of equally intense FN_2^+ and $FN^{15}N^+$ and equally intense F_2N-NH^+ and $F_2N-{}^{15}NH^+$ signals in the labeling experiments suggests that no ^{15}N-isotope effect is operative at appreciable extent in the unimolecular decomposition (9d), which is consistent with the high kinetically effective temperature of the decomposing species.

The observation of a minor $F^{15}N^+$ signal in the CAD spectrum of the $FN^{15}N^+$ ions points to a limited automerization of the $F-N-{}^{15}N^+$ ions into $F-{}^{15}N-N^+$. Recent theoretical results[14] evaluate the energy barrier of this fluorine shift as 282.0 kJ mol^{-1}. This energy is well below the maximum internal energy content of the FN_2^+ ions from (9a)–(9d), evaluated as 521.3 kJ mol^{-1} from the GAUSSIAN-1 enthalpy change of the overall sequence, which does not exclude partial automerization in the ion source. On the other hand, this process could conceivably be related to the CAD event. In fact, the above energy barrier does not exceed the extent of collisional excitation of the FN_2^+ ions, a measure of which is provided by the enthalpy changes associated with the fragmentations observed in the CAD spectrum. In particular, assuming the value of 1214.2 kJ mol^{-1} derived from the GAUSSIAN-1 calculations for the enthalpy of formation of FN_2^+, the $\Delta H°$'s of the processes

$$FN_2^+ \rightarrow F^\bullet + N_2^+$$

$$\rightarrow NF^{\bullet +} + N$$

are evaluated as 368.6 and 672.8 kJ mol^{-1}, respectively, from the experimental enthalpies of formation of the involved dissociation products.

Conclusions

The fluorodiazonium ion is one of the few non-benzenoid diazonium ions actually observed in the solid state and in solution. In the present study, we have provided evidence for its formation in the gaseous phase under typical chemical ionization conditions. The labeling experiments performed and the structurally-diagnostic techniques employed show that in the FN_2^+ ion the two nitrogen atoms are not structurally equivalent. This species can be reasonably identified as the linear $F-N-N^+$, invariably predicted by all the available theoretical studies as the global minimum on the FN_2^+ potential energy surface. The proposed mechanism of formation of the FN_2^+ ions, based on the evidence from FT-ICR and MIKE spectrometry, involves the intermediacy of a F_2N-NH^+ ion. The observation of this species is of interest in that provides the first experimental evidence for stable gaseous F_2N-NX^+ ions, the formation of which in the solid state (X = F) has been so far reported.

Acknowledgment. We thank Mr. F. Angelelli for his assistance in the FT-ICR measurements. The financial support from the Ministero dell'Universitá e della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Ricerche (CNR) is gratefully acknowledged.

IC940627G