Protonated Cyanogen Fluoride. Structure, Stability, and Reactivity of (FCN)H$^+$ Ions

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Gaseous (FCN)H$^+$ ions were obtained by protonation of cyanuric fluoride by strong Brønsted acids such as H_3^+ (D_3^+) and $C_nH_5^+$ ($n = 1, 2$), and their structure and reactivity were examined by FT-ICR mass spectrometry and computational methods at the G2 level of theory. The results show that FCNH$^+$ is considerably more stable than the HFCN$^+$ protomer, the gap amounting to 360 kJ mol^{-1} at the G2 level. The gas-phase basicity (GB) of FCN was estimated by "bracketing" experiments by measuring the efficiency of H$^+$ transfer from FCNH$^+$ to reference bases. Utilizing a general correlation between the rate and the $\Delta G°$ change of the proton-transfer we obtain GB(FCN) = 668.4 ± 10 kJ mol^{-1}, to be compared with the G2 computed GB of 651.8 ± 8 kJ mol^{-1}, both values being referred to N protonation. The reactions of FCNH$^+$ with isolated (C_2H_4) and conjugated (C_6H_6) π systems were also investigated. The ion behaves as a $FC^+ = NH$ electrophile promoting aromatic cyanation, e.g., yielding $C_6H_5CNH^+$ from benzene. Consideration is given to the reaction mechanism and its correlation with solution-chemistry cyanation.

Introduction

Over the past few years cyanogen fluoride (FCN) has been the subject of many theoretical and experimental investigations,[1−7] owing to its role in different fields. Apart from the potential relevance of fluorine compounds to atmospheric chemistry, the study of molecules and radicals produced in process plasmas for electronic devices fabrication is of crucial importance to clarify the mechanisms involved in plasma-based etching processes. It was reported that cyanogen fluoride is one of the major products of etch reactions of Si_3N_4.[1] A further interest in this molecule derives from its use in the synthesis of important compounds as dyes, fluorescent brighteners, and photographic sensitizers.[4]

Although the first attempts at synthesizing and characterizing cyanogen fluoride date back more than sixty years, the knowledge of its properties and reactions in condensed media and in the gas phase has been limited by its difficult preparation, its potentially hazardous and toxic nature, and its instability at room temperature. Indeed, the routes to monomeric gaseous FCN are laborious, the preferred one being the pyrolysis of cyanuric fluoride. At high temperature FCN can also be formed from many procursors, such as cyanogen and carbon tetrafluoride, carbonyl fluoride and nitrogen trifluoride. If ignited by a spark or by a hot wire, FCN explodes and, in the liquid phase, polymerizes very readily at room temperature to the stable trimer, cyanuric fluoride, $F_3C_3N_3$.[8]

The structure and the physical properties of cyanogen fluoride, have been investigated both experimentally[9] and theoretically.[2,3,5−7,10]

Although equilibrium structures, vibrational frequencies, molecular charge distribution, and stability differences between the FCN and CNF isomers were the subject of many experimental studies and were examined at high levels of theory, the only available value of the gas phase basicity of FCN is the one theoretically computed many years ago[10b] and it has been suggested that it can be grossly underestimated.[7] Finally, to the best of our knowledge, no experimental studies have been reported on gaseous protonated cyanogen fluoride and its reactivity.

In this work (FCN)H$^+$ ions were prepared by protonation of cyanuric fluoride and the proton affinity of FCN was reevaluated by the joint application of FT-ICR mass spectrometry and theoretical methods. In addition, selected gas-phase reactions of protonated cyanogen fluoride were investigated and used as a confirmatory probe to establish the structure of the reacting (FCN)H$^+$ ions.

Experimental Section

Materials. The gases were research grade products from Matheson Gas Products, Inc. with a stated purity exceeding 99.95 mol % and were used without further purification. C_6D_6 (99.5 D atoms %) was purchased from Aldrich Chemicals Co. Cyanuric fluoride, 2,4,6-trifluoro-1,3,5-triazine, was obtained from Fluka Chemie AG with a purity in excess of 99 mol %, as established by GC and was used as received.

Instruments. All experiments were performed using a double-cell FTMS 2001 FT-ICR spectrometer equipped with a Odissey data station, from EXTREL (now Finnigan).

Procedure. Protonated cyanogen fluoride was obtained in the source cell by positive chemical ionization, of cyanuric fluoride, $F_3C_3N_3$, using CH_4 as the reagent gas at room temperature and at a pressure of 10^{-7} Torr. The ions at m/z 46, corresponding to (FCN)H$^+$, isolated in the source cell of the spectrometer by broad-band ejection pulses and by the SWIFT method, after crossing the conductance limit plate were thermalized by collisions with the neutral in the second cell. After

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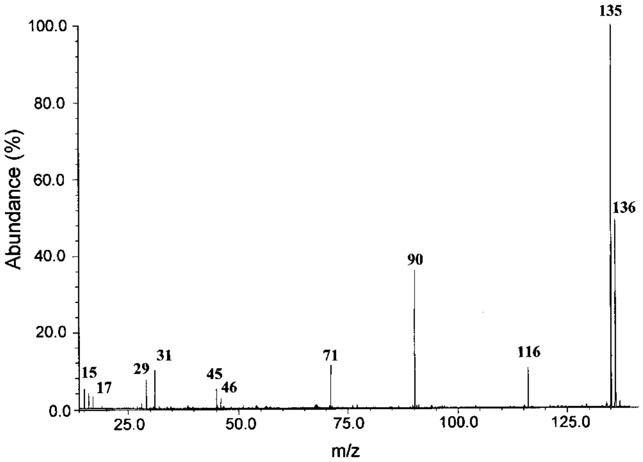


Figure 1. CI/CH_4 spectrum of cyanuric fluoride at 1.3×10^{-7} Torr and 333 K.

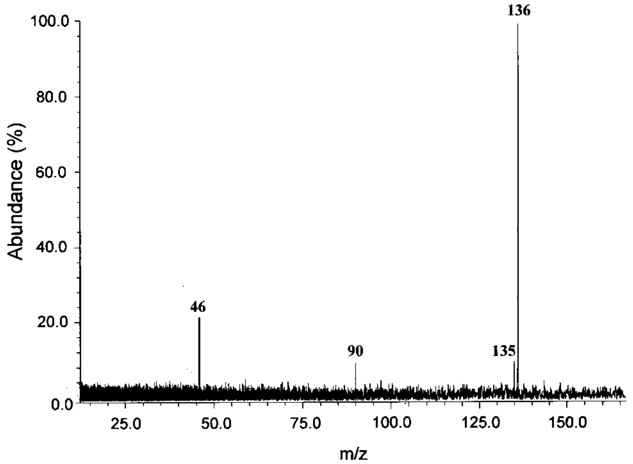


Figure 2. CID spectrum of protonated cyanuric fluoride excited by a low-intensity radio frequency pulse.

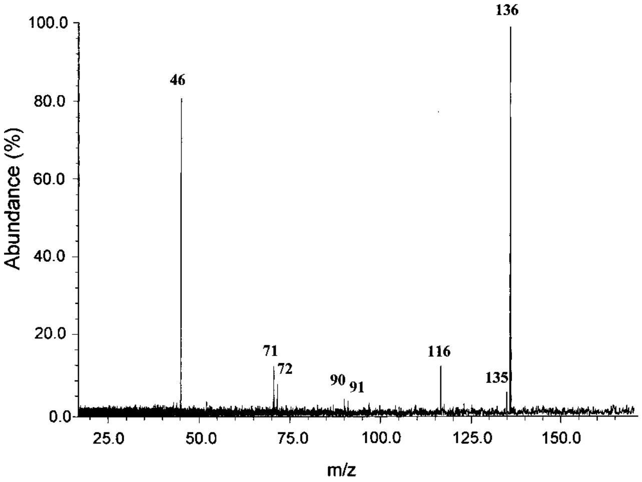


Figure 3. CID spectrum of protonated cyanuric fluoride excited by a high-intensity radio frequency pulse.

a suitable delay (1−3 s), the $(FCN)H^+$ ions were re-isolated and allowed to react with the neutrals, whose pressure was measured by a Bayard-Alpert ionization gauge, calibrated using the known rate coefficient of the $CH_4 + CH_4^+ \rightarrow CH_5^+ + CH_3^\bullet$ reaction as a reference.[11] The readings were then corrected according to a standard method[12] for the relative sensitivity of the gauge to the various gases. The pseudo-first-order rate constants were obtained by plotting the logarithm of the $FCNH^+$ intensities as a function of the time. The bimolecular rate constants were then determined from the number density of the neutral molecules, deduced from the pressure of the gas. Average dipole orientation (ADO) collision rate constants, k_{ADO}, were calculated as described by Su and Bowers.[13] Reaction efficiencies express the ratio of the experimental rate constants, k_{exp}, to the collision rate constants, k_{ADO}. The uncertainty of the rate constants is estimated to be about 30%.

Results

$(FCN)H^+$ Ions. The CI/CH_4 spectrum of $F_3C_3N_3$, illustrated in Figure 1, displays an ion of *m*/*z* 46, corresponding to that of $(FCN)H^+$, whose intensity was found to depend dramatically on the length of the ionization and the postionization delay. Longer times lower its intensity, likely owing to the fast deprotonation of $(FCN)H^+$ by cyanuric fluoride, more basic than FCN.

Whereas the presence of neutral monomeric FCN in the cyanuric fluoride sample was excluded by its GC/MS, FT-IR, and NMR analysis, the following considerations suggest direct formation of $(FCN)H^+$ from protonated $F_3C_3N_3$ excited by the exothermicity of the H^+ transfer from the $C_nH_5^+$ ions. On the basis of the known proton affinities of the corresponding bases, the exothermicity of the proton transfer from CH_5^+ exceeds that from $C_2H_5^+$ by 136.8 kJ mol^{-1}.

In the CI/D_2/$F_3C_3N_3$ experiments the intensity of the $(FCN)D^+$ ions is higher than that of the $(FCN)H^+$ ions formed in the CI/CH_4/$F_3C_3N_3$ experiments under the same conditions, in compliance with the higher exothermicity of D^+ transfer from D_3^+ than of H^+ transfer from $C_nH_5^+$.

Furthermore, protonated cyanuric fluoride, $F_3C_3N_3H^+$, *m*/*z* 136, generated and isolated in the source cell, was allowed to collide with argon in the reaction cell after translational excitation by a suitable radio frequency pulse. At a very low intensity of the radio frequency pulse, protonated cyanuric fluoride dissociates into two fragments of *m*/*z* 90 and 46, corresponding to $F_2C_2N_2^+$ and $(FCN)H^+$, respectively (Figure 2). Using radio frequency pulses of higher intensity, the abundance of the ion at *m*/*z* 46 increases and formation of $(FCN)H^+$ becomes the most important fragmentation pathway (Figure 3). Under these conditions, the ion of *m*/*z* 116 formed from the loss of HF from protonated cyanuric fluoride is also observed.

Reaction of $(FCN)H^+$ with Benzene and Ethylene. The $(FCN)H^+$ ions generated and isolated in the source cell of the ICR spectrometer were reisolated in the reaction cell after a thermalization delay and allowed to react with C_6H_6, C_6D_6, and C_2H_4. These reagents were chosen because in solution $(FCN)H^+$ ions behave as cyanating agents toward aromatic and olefinic π systems, e.g., FCN, ClCN, BrCN, and Cl_3CCN react in solution with benzene in the presence of aluminum chloride to yield benzonitrile,[8d,14] and cyanation of benzene is promoted by protonated Cl_3CCN.[14]

The reaction between gaseous $(FCN)H^+$ ions and benzene gives the ion of *m*/*z* 104, corresponding to $C_7H_6N^+$, as well as $C_6H_7^+$ and $C_6H_6^{\bullet +}$ ions (Figure 4).

To gather further mechanistic evidence, the reactions of $(FCN)D^+$ and $(FCN)H^+$ with C_6H_6 and C_6D_6, respectively, were investigated. The reaction between $(FCN)H^+$ ions and C_6D_6 yields exclusively $C_7D_5HN^+$, no $C_7D_6N^+$ being detected, not even at long reaction times. At short reaction times, the reaction between $(FCN)D^+$ ions and C_6H_6 gives only $C_7H_5DN^+$, $C_7H_6N^+$ ions becoming detectable only at longer reaction times. This is

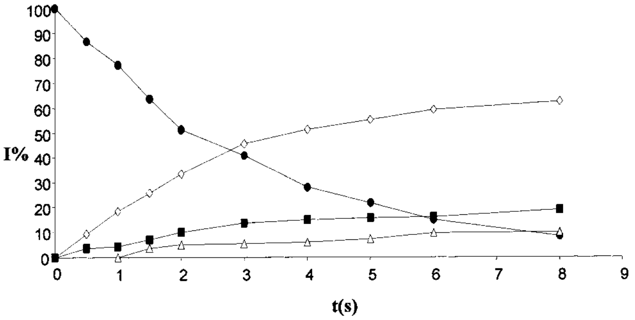


Figure 4. Time profile of the ionic intensities of the reaction between $FCNH^+$ and C_6H_6 P = 2.5 × 10^{-8} Torr: (●) $FCNH^+$; (◇) $C_6H_7^+$; (■) $C_6H_6CN^+$: (△) $C_6H_6^+$.

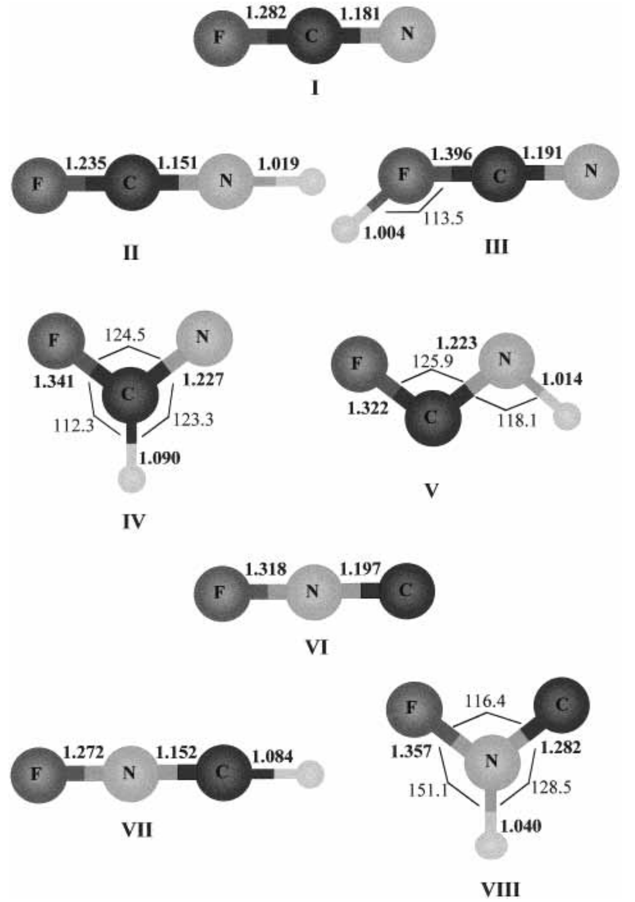


Figure 5. Optimized geometries of the investigated species. Bond lengths are in Å; angles, in deg.

explained by the facile D/H exchange undergone by $C_7H_5DN^+$ with neutral species containing H, such as water, present in the cell.

Computational Results. The experimental results previously described were complemented by a computational study of the gas-phase proton affinities (PA) and basicities (GB) of FCN. The energy values used for such a computation were obtained using the Gaussian-2 theoretical protocol (G2 theory),[16a] which is based on ab initio molecular orbital theory.

The various species involved in this study (CNF, FCN, and the protonated species) were fully optimized at the MP2 level, and their optimized geometrical parameters are illustrated in Figure 5. The corresponding G2 energy values, together with the calculated enthalpies and free energies, are listed in Table 1, whereas the G2 computed values of the gas phase PA and GB are given in Table 2. The accuracy of the G2 method in the calculation of thermochemical quantities, such as the PA of small molecules, is generally within 8 kJ mol^{-1} from experimental results.[16a] On a test set composed of molecules formed by first-row atoms only, for which the experimental PA is well-known, Smith and Radom[16b] found that the average absolute deviation was as low as 2.3 kJ mol^{-1}, with a maximum deviation of 6.9 kJ mol^{-1}.

TABLE 1: Energies, Enthalpies and Free Energies (in Hartree) at 298 K, 1 atm, Calculated at the G2 Level of Theory

	E (0 K)	*H* (298 K, 1 atm)	*G* (298 K, 1 atm)
FCN (**I**)	−192.413382	−192.409571	−192.434955
$FCNH^+$ (**II**)	−192.674186	−192.670140	−192.693101
$HFCN^+$ (**III**)	−192.530996	−192.526345	−192.554538
$FCHN^•$ (**IV**)	−192.974811	−192.970731	−192.999451
$FCNH^•$ (**V**)	−192.970723	−192.966619	−192.995128
CNF (**VI**)	−192.303199	−192.298770	−192.325396
$HCNF^+$ (**VII**)	−192.575477	−192.571317	−192.596626
$CNHF^+$ (**VIII**)	−192.495793	−192.491494	−192.518582

TABLE 2: Gas-Phase Proton Affinities (PA) and Basicities (GB) at 298 K, 1 atm, Calculated at the G2 Level of Theory

	PA (kJ mol^{-1})[a]	GB (kJ mol^{-1})[b]
	FCN	
N protonation	−690.3	−651.8
F protonation	−312.8	−288.0
	CNF	
C protonation	−721.8	−686.2
N protonation	−512.2	−481.3

[a] PA is calculated as the enthalpy of protonation. [b] GB is calculated as the free energy of protonation.

The present computations show that, in FCN, proton binding at nitrogen is largely preferred over binding at fluorine, resulting in the formation of the linear cationic species **II**. No tendency is shown for proton binding at the central carbon.

Conversely, carbon is the preferred protonation site in CNF, again with the formation of a linear cation (strucure **VII**). Furthermore, the FCN species results to be largely more stable than CNF. On the basis of these results, the $(FCN)H^+$ formed in CI experiments is likely to be the cationic species **II**.

Entropy calculations were performed according to the G2 protocol, no special treatment being done for low-frequency modes.

We also calculated the structure and energetics for the neutral radical species that can arise from the neutralization of cation **II**. Two possible species were found to be stable intermediates, corresponding to structures **IV** and **V**. The energy difference between these two neutral species is much smaller than the one for the isomeric cationic structures, with the π-type radical **IV** favored with respect to the σ-type radical **V** by 11.3 kJ mol^{-1}. Spin contamination, while being nonnegligible, is very similar for the two species, the computed value of S^2 being 0.83 and 0.85, respectively.

All the calculations were performed with the Gaussian-94 program suite.[17]

Experimental Evaluation of the GB of FCN. The evaluation of gas-phase basicity by equilibrium methods presupposes the knowledge of the pressure of both neutral reagents involved, which is not achievable in the case of interest. The kinetic method proposed by Cooks et al.[18] is based on the dissociation of proton-bound dimers that are not formed in low-pressure FT-ICR experiments. In the absence of pure, monomeric FCN, the only viable approach to measure the basicity of FCN is afforded by the “bracketing” method,[19] where the gas-phase basicity of the investigated M molecule, GB(M), can be estimated by measuring the efficiency of proton transfer from MH^+ to bases of known GB. The efficiency is high for exoergic proton transfer reactions, falls below the detection limit for strongly endoergic processes, and is low, but still measurable, for reactions endoergic by no more than 4−8 kJ mol^{-1}.

To reduce the uncertainty range of the GB values estimated in this way, the procedure proposed by Bouchoux et al.,[20,21] based on an empirical correlation between the rate of proton transfer and its standard free energy change, was adopted.

Accordingly, the efficiency of proton transfer occurring via a single intermediate

$$[MH^+] + B \underset{k_{-1}}{\overset{k_{\text{coll}}}{\rightleftarrows}} [MHB^+] \xrightarrow{k_1} M + BH^+$$

is correlated to the $\Delta G°$ change of the reaction, namely, to the Δ(GB) difference between the GB of the molecules M and B, by the equation

$$RE = 1/[1 + (k_{-1}/k_1)] = 1/[1 + \exp(\Delta G_{\text{I}}^{\ddagger}/RT)] = 1/[1 + \exp(\Delta G^\circ_{\text{I}} + \Delta G^\circ_{\text{a}})/RT] \quad (1)$$

where RE is the reaction efficiency expressed by the ratio of k_{exp} to k_{coll}, $\Delta G^\circ_{\text{I}}$ is the difference between $\Delta G^\circ_{-\text{I}}$ and $\Delta G^\circ_{\text{I}}$, namely the standard free energy difference of the unimolecular decomposition of the intermediate [MHB^+] back to reactants and forward to the complex, respectively, and $\Delta G^\circ_{\text{a}}$ is the difference between the intrinsic barrier $\Delta G^\circ_{\text{a}} = \Delta G^\circ_{\text{aI}} - \Delta G^\circ_{\text{a-I}}$. Indeed, the activation energy of a given process *i* can be correlated to its free energy change by the equation $\Delta G_i^{\ddagger} = \Delta G^\circ_i - G^\circ_{ai}$, where the latter parameter represents in the intrinsic barrier, that is, the barrier that the reaction would have if it were isoergonic. Therefore, $\Delta G^\circ_{\text{I}} = \text{GB(M)} - \text{GB(B)}$, and $\Delta G^\circ_{\text{I}}$ is the apparent energy barrier for proton transfer, which is expected to be small, and nearly constant, for reactions involving n-type bases.

To deduce GB(M) from a set of experiments, the efficiency data can be fitted into the parametric function:

$$RE = a/\{1 + \exp[b(\Delta G° + c)]\} = a/\{1 + \exp[b(c'' - \text{GB(B)})]\} \quad (2)$$

with GB as a second variable; *a* the normalizing factor, ranging from 0.8 to 1.0; $b = 1/RT^*$, where T^* is the effective temperature that can differ from the experimental temperature owing to a nonequilibrium distribution of the internal energy of the [MBH^+] intermediate; $c'' = \text{GB(M)} + c$, and $c = \Delta G^\circ_{\text{a}}$. The latter was found to be of the same magnitude order of the term $RT^* = 1/b$. Thus, assuming that *c* is precisely equal to RT^*, it is possible to obtain $\text{GB(M)} = c'' - 1/b$.

To evaluate the GB of cyanogen fluoride, $(FCN)H^+$ ions generated in the source-cell by the highly exothermic proton transfer from the $C_nH_5^+$ ions ($n = 1, 2$) to cyanuric fluoride, were allowed to react with n-type bases of different strengths in the analyzer cell.

All the GB values used to establish the correlation between RE and GB are taken from ref 15, to make use of a self-consistent scale based on a single anchoring value.

The collisional efficiencies of proton-transfer reactions from $FCNH^+$ to the reference bases of known GB measured as previously described (Table 3) were fitted to eq 2 as illustrated in Figure 6.

By a best fitting procedure we obtain $a = 1.026$, $b = 0.2817$, $c'' = 671.9$, and $T^* = 427.7$ K; the resulting gas-phase basicity of FCN is 668.4 ± 10 kJ mol^{-1}.

TABLE 3: Efficiencies and Rate Constants of Proton Transfer from $FCNH^+$ to Reference Bases

	$10^9 k_{\text{exp}}$ (molecule^{-1} cm^3 s^{-1})	eff %	GB(B)[a] (kJ mol^{-1})
CH_3OH	1.79 ± 0.30	1	724.5
CCl_3CN	1.84 ± 0.11	1	692.4
CF_3COOH	1.15 ± 0.25	0.85	680.7
CF_3CH_2OH	0.76 ± 0.05	0.49	669.9
C_2H_5Br	0.36 ± 0.004	0.21	669.9
H_2O	0.30 ± 0.13	0.16	659.8
$CF_3CHOHCF_3$	0.03 ± 0.009	0.02	656.0
CH_3Br	<0.01	0	638.0
C_6F_6	<0.01	0	624.4
CH_3Cl	<0.01	0	621.1

[a] From ref 15.

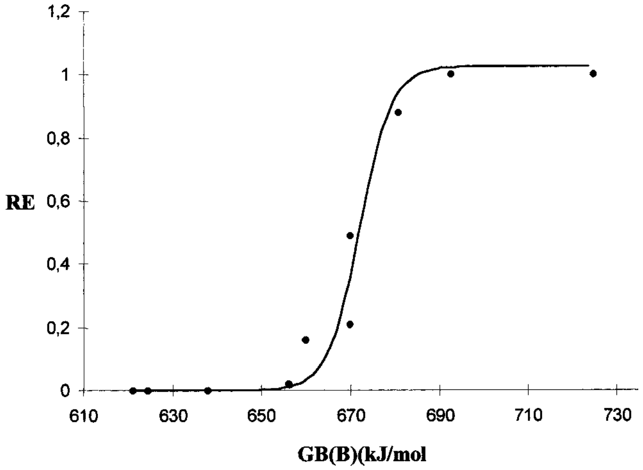


Figure 6. Reaction efficiencies (RE) vs gas-phase basicities for proton transfer between $FCNH^+$ and reference bases.

The present "bracketing" experiments provide the first experimental estimate of the GB (FCN). In evaluating its uncertainty range, several sources of errors, and their propagation, need to be considered. Indeed, apart from the error attached to the measurements proper, a significant contribution arises from the uncertainty affecting the tabulated GB values of the reference bases used. By taking into account the various sources of error, a reasonable estimate of the overall uncertainty of the experimental GB, and hence of the PA of FCN, is of the order of ±10 kJ mol^{-1}. Comparison with the 651.8 ± 8 kJ mol^{-1} GB (FCN) computed at the G2 level of theory reveals a significant discrepancy, 16.6 kJ mol^{-1}, which, however, is not unduly large if one considers the uncertainty range of the two sets of results, in particular the experimental one.

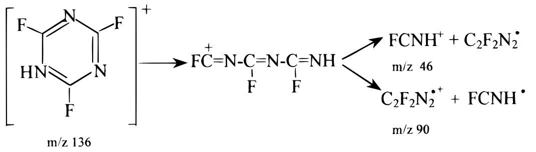
By combining the experimental GB of FCN with the theoretically computed difference between its GB and PA, one arrives at a PA (FCN) value of 706.9 ± 10 kJ mol^{-1}, and from available thermochemical data,[3] to a heat of formation of $FCNH^+$ of 860.1 ± 13 kJ mol^{-1}.

Discussion

The experimental and theoretical results outlined in the previous sections allow structural characterization of the $(FCN)H^+$ ions arising from the CI/CH_4 of cyanuric fluoride that behave as a cyanating agent toward olefinic and aromatic compounds, as well as evaluation of the PA of FCN.

In principle, protonation of cyanuric fluoride by the $C_nH_5^+$-($n = 1, 2$) ions followed by its unimolecular decomposition can give two protomers, i.e., the $FCNH^+$ (**II**) and the $HF{-}CN^+$ (**III**) ions.

Thermochemical considerations based on the theoretically computed heats of formation of the two protomers suggest that the only species emerging from the source cell of the FT-ICR spectrometer is ion **II**. Indeed, protonation at F, yielding $HFCN^+$, is energetically unfavorable by as much as 360 kJ mol^{-1}, the stability difference between the two protomers. Moreover, owing to the very low basicity of the F atom of FCN, it is unlikely that any $HFCN^+$ ion formed would survive fast deprotonation by $C_3F_3N_3$, CH_4, and other bases present in the source cell, which provides strong evidence against the role of protomer **III**. The results of the collisionally induced dissociation experiments suggest that ions **II** arise from a sequence involving N-protonation of $F_3C_3N_3$, ring opening, and subsequent fission of two C−N bonds:



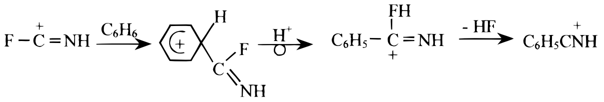
(3)

(4)

Such a process competes with the dissociation (4) that yields the $FCNH^\bullet$ radical.

Passing to the GB of FCN, from the correlation between the effective charges of the C═N bond (δ_{CN}) evaluated by Galabov[6] and the GB of several nitriles[15] (Figure 7), the electron-withdrawing effect of the F atom located in the α position, and reflected by a lower effective bond charge, appears to decrease the basicity of FCN with respect to that of HCN, but not to such a large an extent as previously estimated. In this connection, we note that the GB of FCN obtained in this study exceeds by ca. 70 kJ mol^{-1} the current literature value,[15] independently regarded by other workers as significantly underestimated.[7]

Having addressed the problems related to the formation and the stability of the $(FCN)H^+$ protomers, we now proceed to examine their reaction with a model π system, benzene, yielding protonated benzonitrile. As to the nature of the product, the reaction of $(FCN)D^+$ with C_6H_6 yields $C_6H_5DCN^+$ ions that were reisolated and transferred into the analyzer cell containing NH_3. Deprotonation by ammonia gave only NH_3D^+ ions, conclusively showing that the product of the cyanation process is N-deuteronated benzonitrile rather than an arenium ion that would transfer *both* H^+ and D^+ to the base. Accordingly, the most likely cyanation route is the sequence



(5)

involving electrophilic C-attack on the ring by the $FCNH^+$ protomer **II**, followed by a fast H^+ shift to the F atom and by HF elimination. Overall, the sequence is energetically allowed, being characterized by an exothermicity of ca. 286.5 kJ mol^{-1}.[15]

The reaction of $(FCN)H^+$ with C_6D_6 yields exclusively $C_6D_5CNH^+$ and that of $(FCN)D^+$ with C_6H_6 yields exclusively $C_6H_5CND^+$ ions. These results definitely rule out the role of protomer **III** as a cyanating reagent. Indeed, in the admittedly unlikely hypothesis that $HFCN^+$ ions are present, their reaction with benzene would involve nucleophilic displacement of HF by the arene

$$C_6H_6 + HFCN^+ \rightarrow HF + C_6H_6CN^+ \qquad (6)$$

where the hydron (H or D) initially contained in **III** would *not* be incorporated into the ionic product, contrary to the experimental data.

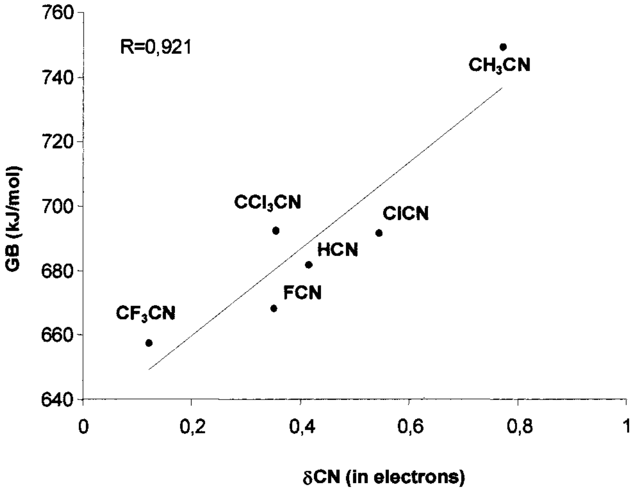


Figure 7. Relationship between the effective charges of the C≡N bond (δ_{CN}) (ref 6) and the gas-phase basicity (ref 15) of a series of nitriles.

Conclusion

The experimental and theoretical evidence from this study shows that the N atom is the most basic site of the FCN molecule, pointing to a large stability gap between the $HFCN^+$ and the $FCNH^+$ protomers. The experimentally and theoretically derived GB of FCN from this study call for a considerable upward revision of earlier estimates, in line with previous suggestions in this direction.[7] The reactivity of the more stable protomer, $FCNH^+$, toward benzene characterizes the ion as a $F{-}{}^{+}C{=}NH$ electrophile, that promotes aromatic cyanation according to a sequence whose first step is the formation of a cyanated arenium ion, followed by H^+ migration from the ipso position of the ring to the F atom, and by the loss of HF, eventually yielding N-protonated benzonitrile. This mechanism establishes a bridge between the gas-phase and the solution chemistry of nitriles in acidic media.[8d,14,22]

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