Experimental Observation of Stable Cyanodiazonium Ions, $NC–N_2^+$

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The elusive cyanodiazonium ion, $NC–N_2^+$, proposed as a transient intermediate in solution, but never directly observed, can be obtained in the gas phase by ionization of a mixture of nitrogen trifluoride and cyanamide, and characterized by collisionally activated dissociation (CAD) mass spectrometry.

Whereas aryldiazonium ions have been well known for a long time and extensively investigated,[1] non-benzenoid diazonium ions are rather elusive species. Long sought for over several decades, only a few of them, such as FN_2^+,[2] $CF_3CH_2N_2^+$ and $(CF_3)_2CHN_2^+$,[3,4] $H_2NN_2^+$,[5,6] MeN_2^+,[7] and $MeON_2^+$[8] have actually been observed in solution, and, in certain cases, isolated and structurally characterized in the solid state. In other circumstances, the experimental findings point to the formation, in the reaction medium, of $X–N_2^+$ ions, which however elude direct observation and unambiguous characterization. Among these, is the cyanodiazonium ion, X = CN, which is proposed by Olah and coworkers[9] to be a transient reactive intermediate in the reaction sequence leading to the formation of aromatic nitriles, eqn. (1).

$$H_2N\text{–}CN + NO^+BF_4^- \xrightarrow[-H_2O]{CH_2Cl_2} [N\text{–}C\text{–}N\text{–}N^+\ BF_4^-]$$

$$\xrightarrow[-N_2]{C_6H_5Me} NC\text{–}C_6H_4Me \qquad (1)$$

However, no evidence for stable, long-lived $NC–N_2^+$ ions could be obtained, even in the absence of the aromatic substrate. Rather, the observation of an exothermic reaction with gas evolution (N_2, BF_3) suggested that the initial formation of $NC–N_2^+$, or of its precursor complex, was followed by rapid nitrogen loss. No further experimental evidence has subsequently been reported on the existence of CN_3^+ ions in solution, nor in the gas phase. Thus, the question is still open as to whether the cyanodiazonium ion does actually reside in a potential well deep enough to allow its direct observation and structural characterization. The present mass spectrometric experiments provide a positive answer to the question.

Gaseous cyanodiazonium ions have been obtained from the ionization of a *ca.* 2:1 mixture of NF_3 and $H_2N–CN$, in a chemical ionization (CI) source ($P \approx 0.1$ Torr).† A well detected signal is observed at *m/z* 54, which is absent in the mass spectra of pure NF_3 and $H_2N–CN$. The collisionally activated dissociation (CAD) spectrum of this ion, shown in Fig. 1, allows the ion to be unambiguously characterized as CN_3^+. In addition to the fragments at *m/z* 26 (CN^+) and 28 ($N_2^{\cdot+}$) which demonstrate the existence of the CN and N_2 moieties, the intence CN_2^+ fragment at *m/z* 40, and the absence of any N_3^+ peak point to a N–C–N–N connectivity. This conclusion is consistent with the results of recent *ab initio* calculations,[10] which identify the cyanodiazonium ion as a minimum on the CN_3^+ potential energy surface, more stable by *ca.* 188 kJ mol^{-1} at the MP2 level of theory than the other conceivable isomer, $C–N–N_2^+$.

The $NC–N_2^+$ ions from the $NF_3/H_2N–CN$ mixture undergo no observable metastable decompositions, giving a blank mass analysed ion kinetic energy (MIKE) spectrum.

Fourier-transform Ion Cyclotron Resonance (FT-ICR) experiments have been performed to investigate the origin of the cyanodiazonium ions observed in the CI plasma. The time dependence of the four ions [$NF^{\cdot+}$ (*m/z* 33), NF_2^+ (52), $NF_3^{+\cdot}$ (71) and $H_2N–CN^{+\cdot}$ (42)] appreciably detected by electron impact (70 eV) ionization of the $NF_3/H_2N–CN$ mixture introduced in the resonance cell of the FT-ICR spectrometer is shown in Fig. 2. The salient feature is that, on increasing the reaction time, no signal is detected at *m/z* 54, suggestive of the formation of CN_3^+. Rather, in the low-pressure domain typical of the ICR cell, the gas-phase ion chemistry of the $NF_3/H_2N–CN$ mixture essentially consists of the fast electron-transfer reactions (2), (3a) and (4), whose standard enthalpies

$$NF_3^{\cdot+} + H_2N\text{–}CN \rightarrow NF_3 + H_2N\text{–}CN^{\cdot+} \qquad (2)$$

$$NF_2^+ + H_2N\text{–}CN \rightarrow NF_2^{\cdot} + H_2N\text{–}CN^{\cdot+} \qquad (3a)$$

$$NF^{\cdot+} + H_2N\text{–}CN \rightarrow NF^{\cdot} + H_2N\text{–}CN^{\cdot+} \qquad (4)$$

changes[11] are calculated as $\Delta H^0_2 = -251$ kJ mol^{-1}, $\Delta H^0_{3a} = -117$ kJ mol^{-1} and $\Delta H^0_4 = -184$ kJ mol^{-1}. In turn, the intermediate $H_2N–CN^{\cdot+}$ radical cation is able to undergo hydrogen-atom abstraction from $H_2N–CN$, and the so formed $(H_2N–CN)H^+$ ions (*m/z* 43) are unreactive in the $NF_3/H_2N–CN$ gaseous mixture. This interpretation of the ionic dependencies displayed in Fig. 2 has been confirmed by independent

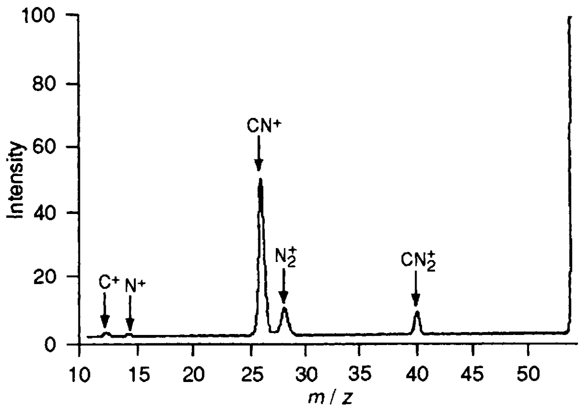

Fig. 1 CAD spectrum of the CN_3^+ ions from the ionization of the $NF_3/H_2N–CN$ gaseous mixture.

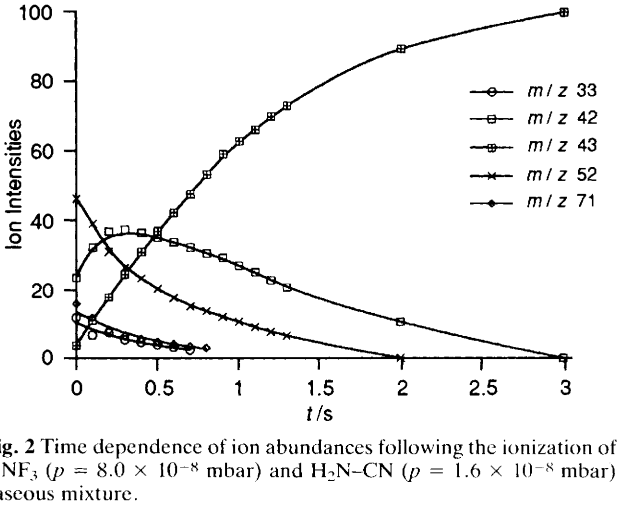

Fig. 2 Time dependence of ion abundances following the ionization of a NF_3 ($p = 8.0 \times 10^{-8}$ mbar) and $H_2N–CN$ ($p = 1.6 \times 10^{-8}$ mbar) gaseous mixture.

experiments involving $NF_3^{\cdot+}$, NF_2^+, $NF^{\cdot+}$, and $H_2N\text{–}CN^{\cdot+}$ ions, isolated by selective-ejection techniques and allowed to react with the gaseous $NF_3/H_2N\text{–}CN$ mixture.

Although it is difficult to reach firm conclusions on the origin of an ionic species observed in a CI plasma, the above results point to the reaction sequence [eqns. (3a)–(c)], as the

$$NF_2^+ + H_2N\text{–}CN \rightarrow NF_2^{\cdot} + H_2N\text{–}CN^{\cdot+} \qquad (3a)$$

$$NF_2^{\cdot} + H_2N\text{–}CN^{\cdot+} \rightarrow [F_2N\text{–}H_2N\text{–}CN^+]_{exc} \qquad (3b)$$

$$[F_2N\text{–}H_2N\text{–}CN^+]_{exc} \rightarrow NC\text{–}N_2^+ + 2HF \qquad (3c)$$

most plausible route to the $NC\text{–}N_2^+$ ion. The fate of the $NF_2^{\cdot}$ and $H_2N\text{–}CN^{\cdot+}$ fragments from reaction (3a) critically depends on the experimental conditions. In the low-pressure domain of the ICR cell ($p \approx 10^{-7}$ mbar) the ion–radical complex conceivably formed from reaction (3b) cannot be collisionally stabilized and hence the two fragments simply fly apart, leaving $H_2N\text{–}CN^{\cdot+}$ as the only detectable ion. By contrast, at the higher pressure of the CI source ($p \approx 0.1$ mbar), the ion–radical complex, partially stabilized by collision with the buffer gas, may undergo loss of two HF molecules, yielding CN_3^+ ions [eqn. (3c)].

Based on the timescale typical of the ZAB-2F spectrometer,[12] a lifetime of at least 10^{-5} s is estimated for the isolated cyanodiazonium ions. Thus, the present gas-phase experiments identify the $NC\text{–}N_2^+$ ion as a stable intermediate, and suggest that its rapid dediazoniation in solution may not reflect an intrinsic instability, but rather the fast displacement of dinitrogen, an excellent leaving group, by the more nucleophilic solvent molecules. This conclusion supports the mechanistic hypothesis by Olah and coworkers[9] on the concerted character of aromatic cyanation *via* the cyanodiazonium ion.

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† The CI, CAD and MIKE experiments were performed with a VG Micromass ZAB-2F mass spectrometer of reversed geometry. Typical operating conditions of the CI source were as follows: gas pressure 0.1–0.2 Torr; source temperature 180 °C; emission current 1 mA; repeller voltage ≈ 0 V; electron energy 100 eV. The MIKE spectra were recorded using an acceleration potential of 8 kV at an energy resolution (fwhm) of 4×10^3. The CAD spectra were taken by admitting He into the collision cell at such a pressure to reduce the main beam intensity to 70% of its initial value.

The FT-ICR experiments were performed with a Bruker Spectrospin APEX TM 47e spectrometer equipped with an external source in addition to the standard internal source. The ICR spectrometer was operated at room temperature, with observation times up to 20 s. For the determination of the gases pressures, the ionization gauge was calibrated on the basis of known reaction rate constants.

References

1 *Superacids*, ed. G. Olah, G. K. S. Prakash and J. Sommer, Wiley, 1985, ch. 4, and references therein.
2 D. Moy and A. R. Young, II, *J. Am. Chem. Soc.*, 1965, **87**, 1889; K. O. Christe, R. D. Wilson, W. W. Wilson, R. Bau, S. Sukumar and D. A. Dixon, *J. Am. Chem. Soc.*, 1991, **113**, 3795.
3 J. R. Mohrig, K. Keegstra, A. Mavenick, R. Roberts and S. Wells, *J. Chem. Soc., Chem. Commun.*, 1974, 780.
4 J. R. Mohrig and K. Keegstra, *J. Am. Chem. Soc.*, 1967, **89**, 5492.
5 A. Mertens, K. Lammertsma, M. Arvanaghi and G. A. Olah, *J. Am. Chem. Soc.*, 1983, **105**, 5657.
6 K. O. Christe, W. W. Wilson, D. A. Dixon, S. I. Khan, R. Bau, T. Metzenthin and R. Lu, *J. Am. Chem. Soc.*, 1993, **115**, 1836.
7 D. Berner and J. F. McGarrity, *J. Am. Chem. Soc.*, 1979, **101**, 3135; J. F. McGarrity and D. P. Cox, *J. Am. Chem. Soc.*, 1983, **105**, 396.
8 G. A. Olah, R. Herges, K. Laali and G. A. Segal, *J. Am. Chem. Soc.*, 1986, **108**, 2054.
9 G. A. Olah, K. Laali, M. Farnia, J. Shih, B. P. Singh, C. J. Shack and K. O. Christe, *J. Org. Chem.*, 1985, **50**, 1338; see also, L. Eberson, R. Nilsson and B. Reitz, *Acta Chem. Scand.*, 1972, **26**, 3870.
10 P. Pyykko and N. Runeberg, *J. Mol. Struct. (Theochem)*, 1991, **234**, 269.
11 All thermochemical data are taken from S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, suppl. 1.
12 J. H. Holmes, *Org. Mass Spectrom.*, 1985, **20**, 1669.