Gaseous Protonated Nitrosyl Fluoride. Experimental and Theoretical Characterization of Two Distinguishable Isomers, HONF\(^+\) and ONFH\(^+\), and Evaluation of the Barrier for Their Interconversion

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The structure, stability, interconversion, and unimolecular decomposition processes of gaseous protonated nitrosyl fluoride, ONF, have been investigated by mass-analyzed ion kinetic energy (MIKE) and collisionally activated dissociation (CAD) mass spectrometry, as well as ab initio GAUSSIAN-1 calculations. Positive evidence has been obtained for the existence of two distinct, not easily interconvertible isomers, NO-NF\(^+\), 1, and ON-FH\(^+\), 3. These two species are distinguishable by both CAD and MIKE spectrometry, whose results are consistent with the theoretical description of the system. The fluoride-protonated isomer 3 is the global minimum on the surface and is more stable than the oxygen-protonated isomer 1 by 70.1 kcal mol\(^{-1}\). Whereas isomer 3 has a low-energy dissociation channel to produce NO\(^+\) and HF, the less stable isomer 1 is trapped in a deep potential well, which prevents both rapid dissociation and isomerization to 3. The GAUSSIAN-1 potential energy diagram explains the distinctly different shapes of the MIKE peaks and the kinetic energy releases (KEKs) associated with the reaction (ONF)H\(^+\) → NO\(^+\) + HF. The loss of HF from 3 gives rise to a narrow peak with a small KEK, while the same reaction from 1 is associated with a dish-topped peak and an exceptionally large KEK (E\(_{1/2}\) = 2.68 eV).

Experimental Section

Materials. Nitrogen fluoride and nitric oxide from Matheson Ltd. and helium from SoL Sud Co. were high-purity research-grade gases used without further purification. Gaseous HF has been obtained from the thermal decomposition (r = 350 °C) of solid potassium hydrogen fluoride, KH\(_2\)F (Aldrich Chemicals Co.) introduced into the source via the direct-insertion probe.

Mass Spectrometric Measurements. MIKE and CAD spectra were recorded using a VG Micromass ZAB-2F instrument of reversed geometry.\(^{10}\) 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 MIKE spectra were recorded using an acceleration potential of 8 kV at an energy resolution ranging from 3 × 10\(^4\) to 6 × 10\(^5\), and represent the average of at least 40 scans. CAD spectra were taken by admitting He into the collision cell at such a pressure to reduce the main beam intensity to 80% of its initial value. The ICR experiments were performed with a Bruker Spectrino APEX 47e spectrometer equipped with an external ion source.

Computational Details. Ab initio quantum-mechanical calculations were performed using a RISC/6000 version of the GAUSSIAN 92 program package.\(^{11}\) The standard internal 6-31G\(^*\),\(^{12}\) 6-311G\(^*\),\(^{13}\) and 6-311G\(^*\) (2df)\(^{12}\) basis sets were employed throughout. Geometry optimizations were performed in the full space of the coordinates by analytical gradient-based techniques\(^{12}\) in the framework of the second-order Moller–Plesset (MP2) perturbation theory,\(^{14}\) 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 (ZPEs) of the various species. Single-point calculations, at the post-SCF level of theory, were performed within the Moller–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\(^{12}\) was employed to obtain the total energies of the various species and the enthalpy change of the investigated processes. This method is generally accepted as a computational procedure which is able to predict or to reproduce thermochemical data to a target accuracy of ±2 kcal mol\(^{-1}\). The performance of this theory in the investigation of gas-phase ionic processes has recently been reviewed and its reliability amply demonstrated.\(^{16}\) In the framework of the GAUSSIAN-1 approach, the total energy of a species, E(G-1), is given by

\[
E(G-1) = E_0 + \Delta E(+) + \Delta E(2df) + \Delta E(QCI) + \Delta E(HLC) + \Delta E(ZPE)
\]

The various correction terms to the MP4(SDTQ)/6-31G** //MP2(FULL)/6-31G* total energy, E\(_0\), are computed as follows: (i) Correction for the inclusion of diffuse sp basis functions:

\[
\Delta E(+) = E(MP4(SDTQ))/6-311+G** // MP2(FULL)/6-31G*) - E_0
\]

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(ii) Correction for the inclusion of higher polarization functions on non-hydrogen atoms:

$$\Delta E(2df) = E(MP4(SDQ)/6-311G^{**}(2df)) / MP2(FULL)/631G^{*} - E_0$$

(iii) Correction for residual correlation effects:

$$\Delta E(QCI) = E(QCl5D(T)/6-31G^{**}) / MP2(FULL)/6-31G^{*} - E_0$$

(iv) Higher-level correction:

$$\Delta E(HLC) = -0.19n_\alpha - 5.95n_\beta$$

where $n_\alpha$ and $n_\beta$ are the number of $\alpha$ and $\beta$ valence electrons, respectively;

$$\Delta E(ZPE) = MP2(FULL)/6-31G^{*}$$

zero-point correction.

**Mass Spectrometric Results**

**Routes to (ONF)H⁺ Ions.** Two different approaches have been successfully employed for the preparation of gaseous (ONF)H⁺ ions under chemical ionization (CI) conditions. The first one is based on the reaction sequence

$$\text{NF}_3 + e^{-} \rightarrow \text{NF}_2^{+} + F^{-} + 2e^- \quad (1a)$$

$$\text{NF}_2^{+} + \text{H}_2\text{O} \rightarrow (\text{NF}_2\text{-OH})^{+} \quad (1b)$$

$$\text{(NF}_2\text{-OH)}^{+} \rightarrow (\text{HONF})^{+} + \text{HF} \quad (1c)$$

Using D₂O, the reaction sequence (1a-c) eventually yields labeled ions that incorporate a D atom. The reaction sequence is supported by the following observations: (i) ionization of NF₃ yields the NF₂⁺ ion ($m/z = 52$) as the most abundant fragment, together with a minor NF⁺ peak ($m/z = 33$). (ii) The (NF₂-OH)⁺ adduct, $m/z = 70$, which shifts to $m/z = 72$ using D₂O, from the exothermic reaction (1b) is readily formed upon ionization of a NF₃/H₂O mixture. (iii) This ion undergoes loss of HF as the only metastable decomposition, thus providing evidence for the occurrence of reaction (1c). The considerable kinetic energy release (KER) of dissociation (1c), measured at the half-height of the metastable peak (Eₜₐₜ) as 1.36 eV, suggests that a proportionately large amount of energy is deposited into the internal degrees of freedom of the (HONF)⁺ fragment, in keeping with its tendency to undergo further metastable decomposition (vide infra). The details of the gas-phase ion chemistry of (NF₂-OH)⁺ ions, in connection with the study of the protonated isotomers of NF₂OH, have been reported in a separate article.¹⁷

Additional evidence for the reaction sequence (1a-c) has been obtained by ICR spectrometry. NF₂⁺ ions have been formed by electron impact ionization of NF₃ in the resonance cell of an ICR spectrometer, isolated by multiple resonance and allowed to react with H₂O. The dependence of the abundances of all the ionic intermediates involved upon the reaction time is depicted in Figure 1. Due to the low-pressure regime of the ICR cell ($P = 5.0 \times 10^{-4}$ Torr), the (NF₂-OH)⁺ ions from (1b), excited by the exothermicity of their formation process, cannot be stabilized by unreactive collisions and immediately dissociate into HONF⁺. Moreover, in the absence of collisional stabilization, only a small but well measurable fraction of the (HONF)⁺ ions from (1c) survives further dissociation into NO⁺ and HF. From Figure 1, an additional sink of the HONF⁺ ions is proton transfer to H₂O. As evidenced from independent double-resonance experiments,
energy release is unprecedented in the metastable fragmentation of singly charged cations. Formation of different isomers has been also investigated by CAD spectrometry of the (ONF)H⁺ populations from reactions (1a–c) and (2), although the relatively low intensity of the (ONF)⁺ ions and the significant contribution from their unimolecular decomposition adversely affect the quality of the CAD spectra. Anyway, formation of structurally different (ONF)H⁺ ions from reactions (1a–c) and (2) emerges clearly from the representative spectra reported in Figure 3. Although evidence of this kind is not conclusive, the fragmentation pattern of the (ONF)H⁺ ions from reaction sequence (1a–c) (Figure 3A), showing the NF⁺ ion at m/z = 33 and the HON⁺ ion at m/z = 31 (which shifts to m/z = 32 from the (ONF)⁺ ion) as the most abundant fragments, together with a structurally diagnostic OH⁺ fragment (m/z = 17), is consistent with structure 1. By contrast, the CAD spectrum of the (ONF)H⁺ ions from (2) (Figure 3B), showing the HF⁺ and the NFH⁺ fragments, at m/z = 20 and 34, respectively, as the most significant ones, accords much better with structure 3.

Theoretical Results

Details of the protonation of ONF have recently been addressed by ab initio quantum mechanical calculations. The question of the existence and the relative stability of the various isomers from protonation at nitrogen, oxygen, and fluorine atoms has been examined at the CISD + Q level of theory, with a double-ζ plus polarization quality basis set. Positive evidence for the existence of four (ONF)H⁺ distinct isomers has been obtained. The fluorine-protonated form was found to be a loosely bound complex of HF and NO⁺, a view supported, inter alia, by the long distance (2.421 Å) between the two groups. This species was found to be much more stable (ca. 70 kcal mol⁻¹) than the three almost degenerate (within 7 kcal mol⁻¹) ions arising from protonation at oxygen and nitrogen.

Whereas the above theoretical results are adequate for predicting the relative stability of the various (ONF)H⁺ protoners, the question of their interconversion barriers has not been addressed. Since the knowledge of these details is crucial for the discussion of the mass spectrometric results, we decided to investigate the (ONF)H⁺ potential energy hypersurface at the GAUSSIAN-1 level of theory.

Optimized geometries, at the MP2(full)/6-31G* level of theory, of the ONF molecule, the four (ONF)H⁺ isomers 1–3, and their interconnecting transition structures TSI–TS4 are shown in Figure 4. The relevant data for the evaluation of the GAUSSIAN-1 energies of the species of interest are given in
Tables 1 and 2. The data given in Table 2 serve to discuss the energetics of the protonation of ONF, and a schematic view of the two-dimensional potential energy diagram of the relative stabiliites of the various (ONF)H⁺ species is given in Figure 5. Protonation at the oxygen atom of ONF gives stable trans and cis isomers, 1a and 1b, the former being more stable by 2.7 kcal mol⁻¹ at the GAUSSIAN-1 level of theory. From Figure 4, and in line with previous findings, comparison of the optimized structures of these protonated forms with that of ONF reveals that O-protonation shortens the F—N bond slightly but lengthens the N—O bond.

From Figure 4, and in full agreement with a previous theoretical study of neutral nitrosyl fluoride, the remarkably consistent between the MP2(FULL)/6-31G* optimized parameters of ONF and the experimental data has to be noted.

CISD ones. In fact, as shown in Figure 4, protonation at the nitrogen atom of ONF results in a tighter F—N bond, whereas the N—O bond length is almost unaffected. Moreover, the increase of the FNO angle by ca. 12° as a consequence of the protonation at the nitrogen atom has to be noted. The interconversion between the O-protonated 1a and the N-protonated 2 requires to overcome a significant activation barrier, computed at the GAUSSIAN-1 level of theory to be 51.1 kcal mol⁻¹ with respect to 1a. This 1,2-hydrogen migration process occurs through the three-center transition structure TS3. The single imaginary frequency associated to the ion, −1656.2 cm⁻¹, refers to the in-plane motion of the hydrogen atom, whose distances from the oxygen and nitrogen atoms are computed as 1.568 and 1.230 Å, respectively.

The ion–dipole complex 3 is obtained by protonation at the fluorine atom of ONF. As previously pointed out, separation of the NO⁺ and HF groups is quite large. From Figure 4, the F—N and F—O bond lengths are computed as 2.286 and 2.566 Å, respectively. From Table 2, ion 3 is by far the most stable among the various (ONF)H⁺ protonates, e.g., it is more stable than 1 and 70.1 kcal mol⁻¹ at the GAUSSIAN-1 level of theory. Moreover, the site PA of the fluorine atom of ONF is computed to be as large as 186.2 kcal mol⁻¹ at 298 K.

From the GAUSSIAN-1 energies of free HF and NO⁺, reported in Table 2, the dissociation enthalpy of ion 3 into these two fragments is computed as 14.6 kcal mol⁻¹. Combining the experimental heats of formation of HF, −65.1 kcal mol⁻¹, and of NO⁺, 235.3 kcal mol⁻¹, with the above computed binding energy, a theoretical heat of formation of 155.6 kcal mol⁻¹ is obtained for ion 3. To evaluate the internal consistency of this value, the enthalpy change of the process

\[
\text{NF}_2^+ + \text{H}_2\text{O} \rightarrow \text{ON—FEH}^+ + \text{HF}
\]

has been calculated using the above-derived heat of formation of 3 and the experimental heats of formation of \(\text{NF}_2^+\), 275 kcal mol⁻¹, \(\text{H}_2\text{O}\), −57.8 kcal mol⁻¹, and HF, −65 kcal mol⁻¹. The obtained value, −126.7 kcal mol⁻¹, can be compared with the enthalpy change obtained on purely theoretical grounds. From the GAUSSIAN-1 total energies of \(\text{NF}_2^+\), −233.583 56 au, and

\[
\text{ON—FEH}^+ + \text{HF}
\]

and

\[
\text{ON—FEH}^+ + \text{HF}
\]
regarded as the route to the oxygen-protonated isomer of ONF, i.e., ion 1. In fact, apart from the evidence provided from the formation process which involves the intermediacy of (NF2—OH)3+, the H—O—N—F connectivity of the ion is consistent with its CAD and, more significantly, with its MIKE spectrum. In fact, owing to the large exothermicity of their formation process, a fraction of HO—NF+ ions from (1a—c) can be formed with sufficient excess internal energy to overcome the barrier corresponding to the transition structure TS2, generating highly excited ions 3 that immediately dissociate into NO* and HF. On the contrary, extensive isomerization of HO—NF+ to ion 2, i.e., the nitrogen-protonated isomer of ONF is prevented by the significantly larger (51.1 to 24.2 kcal mol−1) activation barrier associated to TS3. From Figure 5, it is apparent that the energy difference between TS2 and the separate NO* and HF fragments is large, 3.57 eV, which is reflected in the dish-topped peak shown in Figure 2A. Taking into account the evidence from the study of a large number of simple ions, the experimental Ekip value can be assumed to generally exceed the mean value of the kinetic energy release by 15–20%. Under this assumption, the mean kinetic energy of the fragments would account for 60–70% of the above-computed energy difference, the remaining fraction being partitioned into their rotational and internal degrees of freedom.

The formation of the oxygen-protonated isomer of ONF from reaction sequence (1a—c) is also consistent with the results of the ICR experiments. In fact, the observed proton transfer from HO—NF+ to H2O (PA = 166.5 kcal mol−1) can easily be explained in terms of the calculated proton affinity of the oxygen atom of ONF, as low as 116.1 kcal mol−1. On the contrary, on the basis of the computed proton affinity of the fluorine atom of ONF, 186.2 kcal mol−1, proton transfer from ON—FH+ to H2O would be predicted to be thermochemically forbidden.

Finally, the narrow component of Figure 2A, centered at m/z = 30, can be ascribed to the metastable decomposition of ions 3 formed from the isomerization of HONF+ ions and stabilized by collisional deactivation in the ion source. As a plausible explanation, the isomerization can be envisaged to take place in the ion–molecule complex formed by HONF+ with NF3, whose PA, 136.9 kcal mol−1, happens to be intermediate between the PAs of the oxygen and fluorine atoms of ONF.

Conclusions

The joint application of experimental and theoretical methods provides convincing evidence for the existence of both fluorine- and oxygen-protonated isomers of ONF as distinct species in the gas phase. The protoners are separated by significant activation barriers which prevent their facile interconversion, as well as isomerization to the nitrogen-protonated isomer, whose formation was not detected in this study. The global minimum corresponds to the fluorine protonated isomer 3, ONFH+, which can be viewed as an ion-dipole complex. The oxygen-protonated form 1, HONF+, is less stable by 70.1 kcal mol−1. Whereas isomer 3 has a low-energy dissociation channel to NO* and HF, isomer 1 is trapped in a deep potential well, which prevents both rapid isomerization and dissociation. This peculiar feature of the potential energy surface explains the different KERs associated with the dissociation of 1 and 3, in that HF loss from ON—FH+ gives rise to a narrow peak with a small Ekip (Figure 2B), whereas dissociation of 1 is associated with a dish-topped peak (Figure 2A) and an extraordinarily large Ekip, 2.68 eV. CAD spectrometry has also proved useful to probe the structural differences between ions 1 and 3, and its results are consistent with those from MIKE spectrometry, as well as with the theoretical description of the system.

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References and Notes

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