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Gas-Phase Proton Affinity of Nitric Acid and Its Esters. A Mass Spectrometric and ab Initio Study on the Existence and the Relative Stability of Two Isomers of Protonated Ethyl Nitrate

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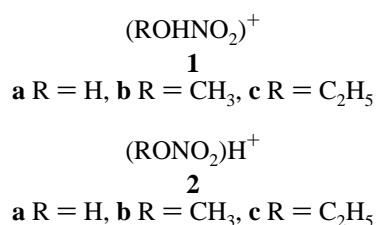
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The protonation of $C_2H_5ONO_2$ has been studied in the gas phase by the joint application of mass spectrometric and ab initio theoretical methods. The MIKE and CAD spectra of $(C_2H_5ONO_2)H^+$ ions from various sources and their reactivity toward selected nucleophiles, investigated by FT-ICR mass spectrometry, point to the existence of two protomers, the $C_2H_5OHNO_2^+$ ion−dipole complex (**1c**) and the covalently bound C_2H_5-$ONOOH^+$ species (**2c**), and to the tendency of the latter to isomerize into **1c** in the presence of neutral C_2H_5-ONO_2. The BE of NO_2^+ to C_2H_5OH, independently measured by the kinetic and the equilibrium methods, amounts to 22.2 ± 2 kcal mol^{-1} at 298 K, leading to a PA of $C_2H_5ONO_2$ of 178.4 ± 2.6 kcal mol^{-1}, referred to the protonation at the ethereal oxygen. The computational results at the G2(MP2) level of theory show that protomers **1c** and **2c** have the same stability at 298 K and that at the same temperature the **2c** → **1c** isomerization is characterized by a $\Delta G°$ change of ca. -3 kcal mol^{-1}. The PA of $C_2H_5ONO_2$ is computed to be 177 ± 2 kcal mol^{-1} at 298 K, irrespective of whether protonation occurs at the ethereal O or at the NO_2 group, in excellent agreement with the experimental value. The results are discussed in connection with the general problem concerning the preferred protonation site and the PA trend along the $RONO_2$ homologous series. It is shown that entirely different factors control the local PA of the RO and the NO_2 groups.

Introduction

Protonated nitric acid has been the subject of extensive structural and thermochemical studies in the gas phase, owing to its intrinsic interest and to its role in atmospheric chemistry.[1−5] Related studies have concerned protonated alkyl nitrates, extensively utilized as charged reagents in gas-phase aromatic nitration.[6−10] Application of structurally diagnostic mass spectrometric techniques has demonstrated the existence of two types of protonated adducts, namely, ion−molecule complexes **1** formed by nitronium ion with water or alcohols and ions **2**,

$$(ROHNO_2)^+$$
$$\mathbf{1}$$
$$\mathbf{a}\ R = H,\ \mathbf{b}\ R = CH_3,\ \mathbf{c}\ R = C_2H_5$$

$$(RONO_2)H^+$$
$$\mathbf{2}$$
$$\mathbf{a}\ R = H,\ \mathbf{b}\ R = CH_3,\ \mathbf{c}\ R = C_2H_5$$

protonated at the nitro group, showing that ions of type **1** are more stable for R = H, CH$_3$.[11,12] Both findings were confirmed by high-level ab initio studies whose results revealed, in addition, a peculiar and counterintuitive trend, namely, the *higher* proton affinity (PA) of nitric acid than of methyl nitrate, 182.5 ± 3 vs 176.9 kcal mol^{-1}.[13,14]

The theoretical prediction is supported by the most recent experimental results, in that flowing-afterglow (FA-SIFT) measurements assign a PA of 177.7 ± 2.3 and 175.0 ± 2.5 kcal mol^{-1} to HNO$_3$ and CH$_3$ONO$_2$, respectively,[15] and the corresponding values from Fourier-transform ion cyclotron resonance (FT-ICR) experiments are 182.0 ± 2.3[16] and 178.0 ± 2.0 kcal mol^{-1}.[17] The larger PA of HNO$_3$ than of CH$_3$ONO$_2$ can be regarded as firmly established, since the experimental
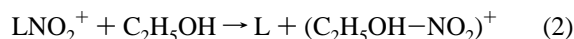
study of the ligand-exchange equilibrium in the H$_2$O/NO$_2^+$/MeOH system gave a ΔPA value of 4.0 ± 1.2 kcal mol^{-1}.[16] However, the current explanation for the phenomenon appears tentative and may benefit from the extension of the study to higher RONO$_2$ homologues to verify whether the observed trend holds for alkyl groups, such as C$_2$H$_5$, characterized by a better σ-donating ability than H and CH$_3$. Furthermore, according to the theoretical results,[14] the stability gap between ions of type **1** and **2** decreases from ca. 20 kcal mol^{-1} for R = H to less than 5 kcal mol^{-1} for R = CH$_3$, suggesting as a definite possibility that the ion of structure **2** could become the most stable isomer for R = C$_2$H$_5$. On the basis of the above considerations, we have undertaken a joint mass spectrometric and theoretical study aimed at ascertaining whether gas-phase protonation of C$_2$H$_5$ONO$_2$ gives isomeric ions of structure **1** and **2**, establishing their relative stability and reevaluating the PA of ethyl nitrate by experimental and theoretical methods more reliable than the "bracketing" technique[18] employed in earlier measurements.[16,19]

Methodology

Structural Analysis. The techniques employed include mass-analyzed ion kinetic energy (MIKE) and collisionally activated dissociation (CAD) spectrometry. The spectra of ionic populations from the protonation of ethyl nitrate with acids of various strength have been compared with those of model ions,

$$AH^+ + C_2H_5ONO_2 \rightarrow A + (C_2H_5ONO_2)H^+ \qquad (1)$$
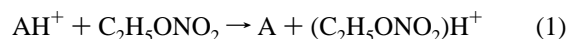
whose structure is expected to correspond exclusively to that of isomer **1**, obtained from ligand-exchange reactions where L denotes a suitable nucleophile.

$$LNO_2^+ + C_2H_5OH \rightarrow L + (C_2H_5OH{-}NO_2)^+ \qquad (2)$$

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TABLE 1: MIKE Spectra of $(C_2H_5ONO_2)H^+$ Ions from Different Reactions

	% intensity[a]				
	reaction 1				reaction 2
m/z	$C_nH_5^+$ (n = 1, 2)	i-$C_3H_7^+$	H_3O^+	$C_2H_5ONO_2^{\bullet+}$	$CH_3OHNO_2^+$, $CH_3ONO_2NO_2^+$
45	5.0 (25.1)	39.8 (82.3)	78.9 (100)	42.7 (40.9)	63.2 (35.9)
46	3.9 (10.5)	15.1 (46.4)	10.3 (13.4)	14.2 (7.1)	100
64	100	100	100 (88.5)	100	

[a] Referred to intensity of the most abundant fragment, taken equal to 100. The values refer to a CH_4 pressure of 0.2 Torr; those in parentheses were measured at a pressure below 0.05 Torr.

Further structural insight has been sought by examining the reactivity of $(C_2H_5ONO_2)H^+$ ions from various sources by FT-ICR mass spectrometry. The ions, formed in the external CI ion source, were isolated by selective ejection of all other cations, collisionally thermalized by Ar, introduced via a pulsed valve,[20] reisolated, and allowed to react with a suitable base/nucleophile, contained at a low stationary pressure in the resonance cell, focusing attention, in particular, on proton vs nitronium ion-transfer reactions.

Thermochemical Measurements. The binding energy (BE) of NO_2^+ to C_2H_5OH has been evaluated by two independent approaches. The first one is the kinetic method,[21] based on the MIKE spectrometry of $[EtOH(NO_2^+)L]$ adducts, where L denotes again a nucleophile of known nitronium ion affinity.[22] The second approach is based on the evaluation of NO_2^+-transfer equilibria by FT-ICR spectrometry.

Results

MIKE Spectrometry. The spectra of $(C_2H_5ONO_2)H^+$ ions from reaction 1 are compared in Table 1 with those of model ions **1c** from reaction 2. The exothermicity of (1), and hence its selectivity, the excess internal energy of the ions formed, and presumably, the isomeric composition of the $(C_2H_5ONO_2)$-H^+ population have been changed by using acids, i.e. $C_nH_5^+$ (n = 1, 2), H_3O^+, and i-$C_3H_7^+$, of different strength, as measured by the PA of their conjugate bases, which spans over a range of some 50 kcal mol^{-1}. The exothermicity of the self-protonation process occurring in $C_2H_5ONO_2$/CI is unknown. However, owing to the relatively high pressure (>0.2 Torr) of neutral ethyl nitrate, the $(C_2H_5ONO_2)H^+$ ions, irrespective of their structure, are likely to undergo extensive conversion into the most stable protomer via fast, exothermic intermolecular proton-transfer processes. Three metastable peaks, all Gaussian-shaped, are observed at *m/z* = 45, 46, and 64 and have been identified as $C_2H_5O^+$, NO_2^+, and $H_2NO_3^+$, on the basis of the isotopic labeling experiments described in the next section. Whereas the relative intensity of the fragments is strongly dependent on the exothermicity of their formation process and especially on the pressure of the reactant gas, their nature is independent of both variables. A salient, structurally diagnostic feature is the absence in the MIKE spectra of model ions **1c** from reaction 2 of the $H_2NO_3^+$ fragment at *m/z* = 64, present in variable abundances in all the spectra of ions from reaction 1.

CAD Spectrometry. Table 2 reports the spectra of the ions of interest, depurated from the metastable contribution to the intensity of the fragments of *m/z* = 46, 45, and 64 by floating the collision cell to -1 kV. As in the MIKE spectra, a conspicuous difference does exist between the CAD spectra of the $(C_2H_5ONO_2)H^+$ ions from reaction 1 and of the **1c** model ions from reaction 2, namely, the absence of the fragment at *m/z* = 64 from the latter ones. The nature of the following fragments has been investigated by labeling experiments, as itemized below.

TABLE 2: CAD Spectra of $(C_2H_5ONO_2)H^+$ Ions from Different Reactions

	% intensity[a]				
	reaction 1				reaction 2
m/z	$C_nH_5^+$ (n = 1, 2)	i-$C_3H_7^+$	H_3O^+	$C_2H_5ONO_2^{\bullet+}$	$CH_3OHNO_2^+$, $CH_3ONO_2NO_2^+$
27	3.3	2.5	1.1	1.6	1.2
28	3.4	1.9	0.6	0.6	0.6
29	20.9	13.6	5.6	4.0	2.5
30	6.0	5.2	1.7	2.6	4.0
31	2.3	4.0	5.0	6.0	6.5
43	3.2	2.9	2.0	2.7	2.6
45	3.9	6.8	9.5	9.9	11.5
46	31.1	48.7	67.1	67.3	69.6
64	24.4	12.9	6.1	3.1	
76	1.5	1.5	1.3	2.2	1.5

[a] Referred to the sum of the intensities of all peaks recorded. Standard deviation ±10%, except in the spectra obtained from $C_nH_5^+$ ions (first column), characterized by a standard deviation of ±20%.

$C_2H_5O^+$, *m/z* = 45. The assignment is consistent with the observation that the m/z ratio increases to 47 and 48 from the fragmentation of $^{13}CH_3^{13}CH_2OHNO_2^+$ and $CD_3CH_2OHNO_2^+$ ions, respectively, produced upon addition of NO_2^+ to the corresponding alcohols. The latter finding suggests, in addition, that the H atom lost in the neutral HNO_2 fragment does not originate from the methyl group.

The identification of the methylene group as the source of the H atom lost is supported by the observation that the fragment at *m/z* = 45 disappears, being replaced by a CH_3CDOH^+ fragment of *m/z* = 46, isobaric with NO_2^+, from the adduct **1c** obtained upon addition of NO_2^+ to CH_3CD_2OH. The mixed **1c/2c** population from the protonation of $C_2H_5ONO_2$ with H_3O^+ displays a CH_3CHOH^+ fragment of *m/z* = 45, which disappears if D_3O^+ is used instead of H_3O^+. This can be rationalized assuming that in the case of deuteration a CH_3CHOD^+ fragment is formed, which again happens to be isobaric with the NO_2^+ ions, a major peak in the CAD spectrum. The above observations strongly suggest that the fragment of *m/z* = 45 from $(CH_3CH_2ONO_2)H^+$ has the CH_3CHOH^+ structure and arises exclusively from isomer **1c**.

NO_2^+, *m/z* = 46. The assignment is based on the observation that the *m/z* ratio of the fragment from ^{13}C- or D-labeled precursors remains unchanged.

$H_2NO_3^+$, *m/z* = 64. The fragment is formed only from the ions prepared according to reaction 1, and its *m/z* ratio increases to 65 from the dissociation of the $(C_2H_5ONO_2)D^+$ precursor.

CH_3O^+, *m/z* = 31. The *m/z* ratio increases to 32 when the parent contains two ^{13}C atoms, and the same mass shift is observed in the fragment from the $(CH_3CH_2ONO_2)D^+$ precursor. The H atoms of the CH_3O^+ fragment do not originate from the methyl group, as suggested by the *m/z* ratio of 31 of the peak observed in the CID spectrum of $CD_3CH_2OHNO_2^+$.

MIKE Spectra of NO_2^+ Bound Dimers. The spectra of the adducts obtained by CI of suitable L_1/L_2 ligand pairs using NO_2 or CH_3ONO_2 as a reactant gas are reported in Table 3.

TABLE 3: MIKE Spectra of Nitronium-Ion-Bound and Proton-Bound Adducts

ligand pairs, L_1/L_2		fragments (m/z), I%	
$CH_3NO_2/C_2H_5OH^a$	$CH_3NO_2NO_2^+$ (107) = 82.6%	$C_2H_5OHNO_2^+$ (92) = 17.4%	
$CH_3NO_2/C_2D_5OD^a$	$CH_3NO_2NO_2^+$ (107) = 82.7%	$C_2D_5ODNO_2^+$ (98) = 17.3%	
$C_2H_5ONO_2/CH_3NO_2^b$	$CH_3NO_2H^+$ (62) = 1.9%	$(C_2H_5ONO_2)H^+$ (92) = 17.8%	$CH_3NO_2NO_2^+$ (107) = 80.3%
$C_2H_5ONO_2/CD_3NO_2^b$	$CD_3NO_2H^+$ (65) = 0.9%	$(C_2H_5ONO_2)H^+$ (92) = 17.7%	$CD_3NO_2NO_2^+$ (110) = 81.4%
$C_2H_5NO_2/C_2H_5OH^c$	$C_2H_5NO_2H^+$ (76) = 23.2%	$C_2H_5OHNO_2^+$ (92) = 2.0%	$C_2H_5NO_2NO_2^+$ (121) = 74.8%
$C_2H_5NO_2/C_2D_5OD^c$	$C_2H_5NO_2D^+$ (77) = 27.9%	$C_2D_5ODNO_2^+$ (98) = 3.9%	$C_2H_5NO_2NO_2^+$ (121) = 68.2
$C_2H_5ONO_2/C_2H_5NO_2^b$	$C_2H_5NO_2H^+$ (76) = 31.1%	$(C_2H_5ONO_2)H^+$ (92) = 1.0%	$C_2H_5NO_2NO_2^+$ (121) = 67.9%

^{a} NO_2^+/CI. ^{b} CH_4/CI. ^{c} CH_3ONO_2/CI.
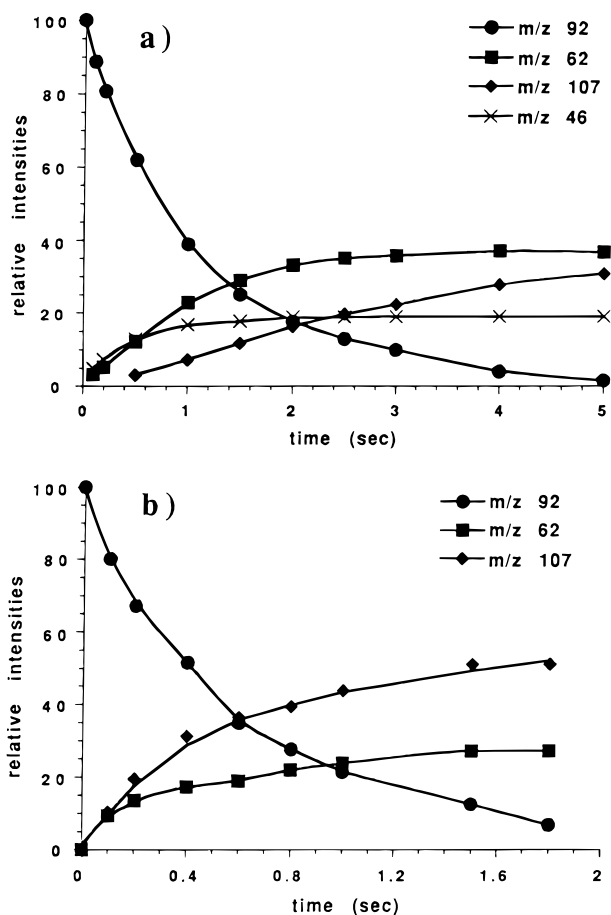
**Figure 1.** (a) Time profile of the ionic intensities in the reaction of $(C_2H_5ONO_2)H^+$, $m/z = 92$, with CH_3NO_2, yielding NO_2^+, $m/z = 46$, $(CH_3NO_2)H^+$, $m/z = 62$, and $(CH_3NO_2)NO_2^+$, $m/z = 107$. (b) Same, after thermalization of $(C_2H_5ONO_2)H^+$ ions (see text).

Certain adducts, e.g. in the case of the CH_3NO_2/C_2H_5OH pair, give only $L_1NO_2^+$ metastable fragments, whereas in other systems the dissociation of the adducts gives, in addition, fragments corresponding to protonated ligands. Application of the kinetic method[21] and the calibration reported in an extensive study on NO_2^+ bound dimers[22] lead to a $\Delta G°$ difference of 0.7 $\pm$ 0.1 and 1.7 $\pm$ 0.1 kcal mol^{-1} for the CH_3NO_2/C_2H_5OH and the $C_2H_5NO_2/C_2H_5OH$ pairs, respectively. Under the usual assumption that $\delta(\Delta G°) \cong \delta(\Delta H°)$ and utilizing the available NO_2^+ BE scale,[22] one arrives at a NO_2^+ BE of C_2H_5OH of 22.1 and 22.3 kcal mol^{-1} from the dissociation of CH_3NO_2-$(NO_2^+)C_2H_5OH$ and $C_2H_5NO_2(NO_2^+)C_2H_5OH$, respectively. Whereas the internal consistency of the results is quite satisfactory, the absolute error bar is considerably larger,[22] and the NO_2^+ BE of C_2H_5OH from the kinetic method can be taken as 22.2 $\pm$ 2 kcal mol^{-1}.

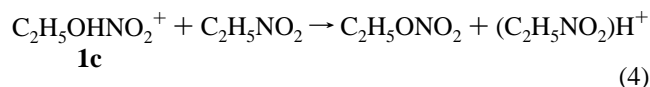**Structural Evidence from FT-ICR Spectrometry.** The $(C_2H_5ONO_2)H^+$ ions from the protonation (1) of ethyl nitrate by $C_nH_5^+$ ions ($n = 1, 2$) when isolated and allowed to react

with CH_3NO_2 without preliminary thermalization undergo predominant H^+ transfer, accompanied by NO_2^+ transfer and formation of free NO_2^+, as illustrated in Figure 1a. On the other hand, if thermalized by collision with Ar and reisolated after 3−5 s, they undergo predominant NO_2^+ transfer to CH_3NO_2, whereas H^+ transfer is depressed and dissociation into NO_2^+ suppressed (Figure 1b). These results suggest that two isomeric cations of $m/z = 92$ are formed in the ion source, one (presumably **2c**) reacting as a protonating species and the other one (presumably **1c**) reacting as a nitrating agent, a behavior previously noted in the study of isomeric $(CH_3ONO_2)H^+$ ions.[10] In the relatively long time (>3 s) required for collisional thermalization of the ions, pumping down the cell, and reisolation of the ions, they can interact with neutral ethyl nitrate, bleeding in traces from the external source, and ions **2c** can undergo proton transfer to $C_2H_5ONO_2$, yielding **1c**. As a consequence, the fraction of the latter isomer increases, with a corresponding enhancement of the nitration channel efficiency. To take place at any significant rate the proton-transfer process must be exoergonic, which entails a standard free energy decrease in the **2c** → **1c** conversion.

Application of the FT-ICR Equilibrium Method. CH_3O-$(NO_2)_2^+$ ions, produced by CH_3ONO_2/CI in the external ion source, were introduced into the resonance cell containing $C_2H_5OH/C_2H_5NO_2$ mixtures of known composition. The nitrated adducts formed via NO_2^+ transfer from $CH_3O(NO_2)_2^+$ to both ligands were allowed to equilibrate according to the ligand-exchange reaction

$$C_2H_5OHNO_2^+ + C_2H_5NO_2 \rightleftharpoons$$
$$m/z = 92$$

$$C_2H_5OH + C_2H_5NO_2NO_2^+ \quad (3)$$
$$m/z = 121$$
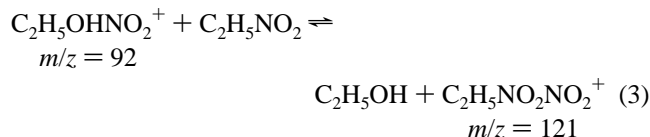
Owing to the occurrence of the competitive process

$$C_2H_5OHNO_2^+ + C_2H_5NO_2 \rightarrow C_2H_5ONO_2 + (C_2H_5NO_2)H^+$$
$$\mathbf{1c}$$
$$(4)$$

a steady-state condition, rather than a true equilibrium, is attained, and the i_{92}/i_{121} intensity ratio, which remains constant over a significant time interval allows one to derive only an apparent value (K_{app}) of the equilibrium constant K_3. Application of the steady-state approximation leads to the expression

$$K_3 = \frac{K_{app}}{1 - k_4 i_{92}/k_3 i_{121}}$$

where the intensity ratio is that measured in the steady-state condition. An approximate value of k_3, $(6.7 \pm 3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, has been estimated from the initial rate of reaction 3, and k_4 has been evaluated from independent experiments utilizing isolated ions **1c** to be $(1.8 \pm 1) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. From these values and the i_{92}/i_{121} ratios

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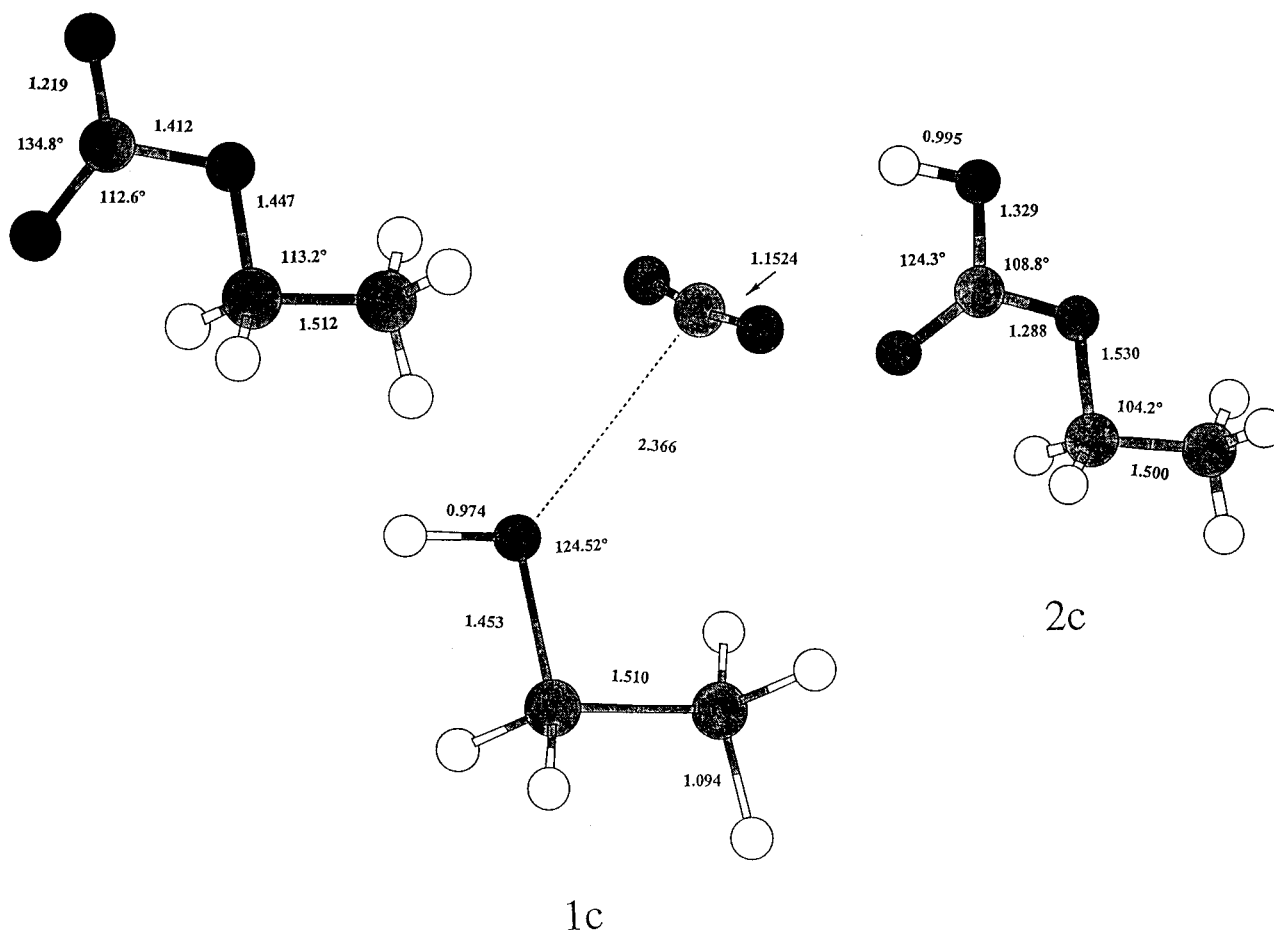**Figure 2.** Geometries of neutral $C_2H_5ONO_2$ (top left) and of protomers **1c** and **2c** optimized at the MP2 (full)/6-31G(d) level of theory. Distances in angstroms, angles in degrees.

from a set of experiments, we obtain $K_3 = (3.7 \pm 1) \times 10^{-2}$ at 300 K, and hence $\Delta G_3^\circ = 2.0 \pm 0.2$ kcal mol^{-1}.

Utilizing the NO_2^+ BE to $C_2H_5NO_2$, and under the customary assumption that $\Delta G_3^\circ \simeq \Delta H_3^\circ$, one obtains a BE value of ca. 22 kcal mol^{-1} for the $C_2H_5OHNO_2^+$ complex **1c**, in excellent agreement with the 22.2 ± 2 kcal mol^{-1} value from the kinetic method reported in the previous section.

Computational Results. The presumably small stability gap between protomers **1c** and **2c** calls for the application of high-level computational methods. At the same time, one has to take into account the relatively large number of atoms in the $[C_2,H_6,N,O_3]^+$ system, as well as the most likely existence of many conformers of comparable stability. A reasonable compromise has been stricken as follows. The geometries of the conformers of ethyl nitrate, **1c**, and **2c** were optimized at the MP2(full)/6-31G(d) level of theory by using a RISC/6000 version of the Gaussian 94 package of programs.[23] The optimized geometries of the lowest energy conformers of ethyl nitrate, **1c**, and **2c** found are depicted in Figure 2. The thermochemical data of interest were obtained by employing the Gaussian 2 procedure with second-order, rather than fourth-order, Møller—Plesset theory (G2MP2).[24] Such a procedure was recently shown to give PA values whose accuracy is comparable to that typical of the G2 theory.[25] In the framework of the procedure adopted the total energy is given by

$$EG2(MP2)(0\ K) = E[QCISD(T)/6\text{-}311G(d,p)] +$$
$$E[MP2/6\text{-}311+G(3df,2p)] - E[MP2/6\text{-}311G(d,p) +$$
$$ZPE[HF/6\text{-}31G(d)] + HLC$$

To this end, single-point calculations were performed for ethyl nitrate, ions **1c** and **2c**, ethanol, and NO_2^+ by using a DEC-

TABLE 4: G2(MP2) 0 K Absolute Energies and 298 K Absolute Enthalpies (Hartree/Molecule)

| species		$E_{G2MP2}(0\ K)$	$H_{G2MP2}(298\ K)$
$C_2H_5ONO_2$	C_s	−358.994 27	−358.987 095
$C_2H_5OHNO_2^+$ (**1**)	C_s	−359.275 72	−359.266 645
$C_2H_5ONO_2H^+$ (**2**)	C_s	−359.274 46	−359.266 825
C_2H_5OH	C_s	−154.760 51	−154.755 20
NO_2^+	$D_{\infty h}$	−204.479 865	−204.476 305

AXB-OSF/1 Revision C2 version of the Gaussian 94 program. The 0 K total energies of the species of interest, G2(MP2)(0 K), were corrected to 298 K by adding translational, rotational, and vibrational contributions, the last term being calculated by standard statistical-mechanistic formulas[26] using the scaled (0.8929) HF/6-31G(d) vibrational frequencies. The G2(MP2)-(298 K) energies derived in this way (Table 4) were corrected to standard enthalpies by assuming ideal gas behavior. The results show that protomer **1c** is only marginally more stable than **2c** at 0 K, the computed enthalpy difference being as small as 0.8 kcal mol^{-1}. However, even such a difference vanishes at 298 K, owing to the vibrational contribution, which is larger for the ion—molecule complex **1c**. The absolute entropies for the species **1c** and **2c** were calculated by using standard statistical-mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to MP2(full)/6-31G-(d) optimized geometries. By taking into account the enthalpic and entropic values calculated for the two protomers, the ΔG° change for the **2c** → **1c** isomerization is found to be −3 kcal mol^{-1} at 298 K, showing that the process is marginally exoergic.

As to the PA of ethyl nitrate, we obtain a value of 177.0 kcal mol^{-1} for both the alternative protonation sites, with an

estimated error bar of ± 2 kcal mol^{-1}. Finally, from the computed energies of NO$_2^+$, ethanol, and **1c**, we obtain a C$_2$H$_5$-OH$-$NO$_2^+$ BE of 22.2 kcal mol^{-1} at 298 K.

Discussion

Structure, Fragmentation, and Interconversion of the Isomers. The mutually supporting evidence from MIKE, CAD, and FT-ICR experiments points to the existence of two (C$_2$H$_5$-ONO$_2$)H$^+$ isomers and allows a definition of their salient features. The MIKE spectra of the ions **1c** from process 2 display no metastable fragment at $m/z = 64$, present instead in variable abundances in the spectra of the mixed populations from reaction 1. CAD spectrometry, complemented by experiments involving ^{13}C and d-labeled species, provides convincing evidence for the existence of two isomers. Model ions **1c** display a dissociation pattern dominated by the NO$_2^+$ fragment, $m/z = 46$, i.e. the ligand loss typical of an ion$-$molecule complex. Another significant process leads to formation of the

$$CH_3-CH\overset{+}{\underset{H}{}}\overset{\displaystyle H}{\underset{\displaystyle O}{}}NO \longrightarrow CH_3CHOH^+ + HNO_2 \quad (5)$$

$$\mathbf{1c}$$
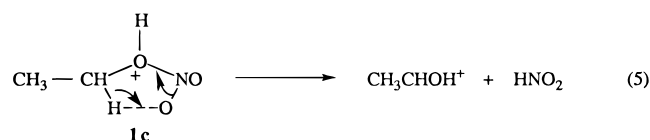
C$_2$H$_5$O$^+$ fragment, $m/z = 45$, probably via a cyclic transition state, as suggested by the observation that the H atom lost in the neutral fragment originated exclusively from the methylene group. Significantly, protonated acetaldehyde is the most stable among (C$_2$,H$_5$,O)$^+$ isomers.[18] Finally, **1c** dissociates into a charged fragment of $m/z = 31$, identified as (C,H$_3$,O)$^+$ according to the results obtained with d-labeled species, which indicate, in addition, that the methyl group is lost in the neutral fragment(s). A plausible hypothesis to account for such selective loss involves again a five-membered cyclic transition state.

$$H_3C\overset{\displaystyle CH_2}{}\overset{+}{OH} \longrightarrow CH_2OH^+ + CH_3ONO \quad (6)$$
$$O-NO$$
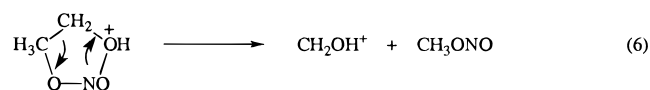
The only, conspicuous feature of isomer **2c** is the fragmentation into H$_2$NO$_3^+$, $m/z = 64$. The results obtained using d-labeled species suggest a cyclic transition state, leading to the formation of the most stable isomer of protonated nitric acid.[11,16]

$$H_2C\overset{\displaystyle H}{}\overset{+}{O}\overset{\displaystyle H}{}\longrightarrow H_2NO_3^+ + C_2H_4 \quad (7)$$
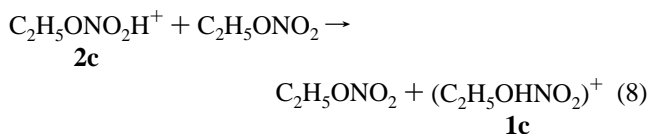$$H_2CNO$$
$$O$$
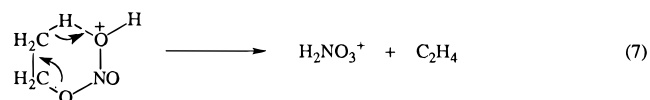
Although isomer **2c** cannot be prepared in the pure state, being invariably formed together with **1c** from process 1, several criteria can be adopted for its characterization by CAD spectrometry in the mixed populations. Assuming that the fragment of $m/z = 64$ originates exclusively from **2c**, whereas those of $m/z = 31$ and 45 originate only from **1c**, one can utilize the intensity ratio $R_1 = i_{64}/i_{45}$, or $R_2 = i_{64}/i_{31}$. Referring to the most intense fragment in the CAD spectra (Table 2), one notices that the abundances of the peaks of $m/z = 64$ (H$_2$NO$_3^+$) and 29 (protonated ethylene) follow parallel trends, suggesting that both originate from **2c**, whereas NO$_2^+$, $m/z = 46$, most likely originates only from the ion$-$molecule complex **1c**. Thus, a third ratio, $R_3 = (i_{29} + i_{64})/i_{46}$ can be used to evaluate the **2c** abundance in the mixed populations from different sources. To

TABLE 5: Structurally Diagnostic Intensity Ratios of the CAD Spectra

	reaction 1				reaction 2
intensity ratios[a]	C$_n$H$_5^+$ (n = 1, 2)	i-C$_3$H$_7^+$	H$_3$O$^+$	C$_2$H$_5$ONO$_2$$^{\bullet+}$	CH$_3$OHNO$_2^+$, CH$_3$ONO$_2$NO$_2^+$
i_{64}/i_{45}	100	30	10	5	0
i_{64}/i_{31}	100	30	11	5	0
$(i_{29} + i_{64})/i_{46}$	100	37	12	7	2.5

[a] The ratios are normalized with respect to that measured in the (C$_2$H$_5$ONO)H$^+$ ions from reaction 1 performed with C$_n$H$_5^+$ ions.

facilitate comparison, the ratios typical of the ions from the protonation by C$_n$H$_5^+$ ions are used as the reference standards. Inspection of the Table 5 demonstrates the satisfactory consistency of the results from three different intensity ratios, which indicate that the abundance of isomer **2c** increases in the populations from reaction 1 in the following order: self-protonation < protonation by H$_3$O$^+$ < protonation by i-C$_3$H$_7^+$ < protonation by C$_n$H$_5^+$. The exothermicity of (1) is not the only factor that controls the abundance of **2c**; for example, the latter is *higher* from the almost thermoneutral (vide infra) protonation of C$_2$H$_5$ONO$_2$ by i-C$_3$H$_7^+$ than from the appreciably exothermic (some 10 kcal mol^{-1}) protonation by H$_3$O$^+$. The key factor seems to be the ability of the bulk gas present in the CI source to promote **2c** $\rightarrow$ **1c** conversion. For example, the abundance of **2c** appears particularly low in the population from the self-protonation process occurring in C$_2$H$_5$ONO$_2$/CI, where the initially formed **2c** isomer undergoes the intermolecular isomerization

$$C_2H_5ONO_2H^+ + C_2H_5ONO_2 \rightarrow$$
$$\mathbf{2c}$$
$$C_2H_5ONO_2 + (C_2H_5OHNO_2)^+ \quad (8)$$
$$\mathbf{1c}$$

whose occurrence is independently supported by the FT-ICR results, illustrated in a previous section. The latter USOHs demonstrate a fundamental difference in the reactivity of **1c** and **2c** toward bases/nucleophiles, showing that isomer **1c** reacts predominantly as a nitrating agent, whereas **2c** behaves as a Brønsted acid, consistent with their structural assignment.

The theoretical results reported in the previous section support the conclusions based on the mass spectrometric evidence. In particular, the theoretical description of the structure of **1c** and **2c**, illustrated in Figure 2, is consistent with the experimental fragmentation pathway and the observed reactivity of the two protomers. The optimized geometry of **1c** characterized the adduct as an ion$-$dipole complex, with a large separation, 2.366 Å, and hence a relatively weak coordination of the monomers, which explains the nitrating ability of **1c** with the occurrence of simple ligand-exchange reactions and the extensive loss of NO$_2^+$ noted in MIKE and CAD spectra with the fission of the relatively weak ion$-$dipole bond. By contrast, the structure of **2c** characterizes the ion as a protonating, rather than a nitrating, species, as apparent from its optimized gometry illustrated in Figure 2. The theoretical results help explain the occurrence of **2c** $\rightarrow$ **1c** isomerization via reaction 8, since the computed ΔG°_8 change, -3.1 kcal mol^{-1}, corresponds to a value on the order of 200 for the K_8 equilibrium constant at 298 K. From a kinetic standpoint, this implies that the depletion rate of **2c** by proton transfer to ethyl nitrate, yielding **1c**, largely exceeds the rate of the inverse process. Since the *intrinsic* kinetic barrier for proton transfer between unhindered n-type bases is generally low in the gas phase,[27] reaction 8 is expected to be an efficient intermolecular route for **2c** $\rightarrow$ **1c** isomerization in gaseous media containing ethyl nitrate. On the other hand, the mass spectro-

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TABLE 6: Unscaled RHF/6-31G* Harmonic Frequencies

frequencies (cm^{-1})	symmetry	IR intensities (km/mol)	frequencies (cm^{-1})	symmetry	IR intensities (km/mol)
			$C_2H_5ONO_2$		
108.9	A″	0.9	1419.3	A″	1.3
131.5	A″	0.9	1519.0	A′	138.4
274.6	A″	0.5	1572.1	A′	101.6
421.3	A″	7.8	1612.4	A′	154.8
643.7	A′	17.0	1628.3	A″	5.3
828.3	A′	2.6	1642.4	A′	8.2
890.2	A″	5.1	1672.2	A′	2.4
917.8	A″	29.2	1906.0	A′	722.5
1003.0	A′	6.2	3224.4	A′	16.2
1103.0	A′	15.3	3284.0	A′	1.3
1187.4	A′	263.9	3297.4	A′	34.7
1252.7	A′	24.3	3301.5	A″	10.9
1296.8	A″	6.2	3349.3	A″	30.9
			$C_2H_5OHNO_2^+$		
22.3	A″	0.7	1418.8	A′	127.1
58.1	A″	1.2	1426.9	A″	1.0
89.3	A′	9.0	1551.3	A′	1.8
185.4	A″	0.2	1605.3	A′	17.4
224.9	A′	21.1	1634.7	A″	16.4
293.0	A″	1.1	1648.9	A′	0.9
391.7	A″	148.2	1677.1	A′	1.4
462.0	A′	7.6	1685.2	A′	0.8
696.2	A′	79.8	2661.1	A″	812.1
762.1	A′	22.5	3201.4	A′	25.4
883.8	A″	0.2	3248.6	A′	30.6
953.0	A′	25.8	3256.5	A″	18.9
1135.5	A′	81.7	3301.0	A′	13.8
1172.4	A′	23.7	3302.5	A″	51.1
1291.5	A″	7.3	4081.1	A′	107.7
			$C_2H_5ONO_2H^+$		
88.0	A″	0.1	1381.5	A′	619.8
149.7	A″	7.6	1398.0	A″	4.4
216.1	A″	2.0	1534.8	A′	21.4
271.1	A″	1.3	1572.7	A′	16.8
378.8	A′	30.9	1615.2	A″	14.1
525.2	A′	74.9	1633.8	A′	3.0
568.7	A″	183.4	1634.9	A′	14.5
753.8	A′	1.4	1679.7	A′	78.0
870.0	A″	25.2	2005.2	A′	388.8
890.5	A″	4.2	3236.1	A′	0.6
908.8	A′	49.3	3309.8	A′	0.1
1031.1	A′	63.2	3317.5	A′	2.4
1135.7	A′	75.8	3332.4	A″	2.4
1235.6	A′	13.9	3397.9	A″	0.9
1271.7	A″	10.7	3884.3	A′	383.3

metric evidence suggests that intramolecular **2c** → **1c** isomerization is comparatively slow. Owing to the complexity of the system, no attempts at evaluating the height of the barriers to the intramolecular isomerization process have been performed.

PA of Ethyl Nitrate. The present results, pointing to the existence of two protomers and to the tendency of **1c** to react with bases/nucleophiles as a nitrating rather than a protonating agent, question the applicability of the equilibrium and the bracketing technique to the measurement of the PA of C_2H_5-ONO_2, suggesting that the available literature data should be taken with reservation.[28] Under the circumstances, an indirect approach utilizing the NO_2^+ BE to C_2H_5OH appears the least unsatisfactory. By combining the BE from the kinetic and the equilibrium method, 22.2 ± 2.6 kcal mol^{-1}, with the heats of formation of H$^+$, NO_2^+, C_2H_5OH, and $C_2H_5ONO_2$, one obtains PA($C_2H_5ONO_2$) = 178.4 ± 2.6 kcal mol^{-1}. Such large error bars and the correspondingly high uncertainty of the PA of CH$_3$-ONO_2, 178 ± 2 kcal mol^{-1}, make it difficult to ascertain the PA trends of homologous $RONO_2$ compounds. Fortunately, tighter error margins characterize the PA *differences* calculated from BE differences. For example, in the case of interest, PA-

($C_2H_5ONO_2$) − PA(CH_3ONO_2), denoted as ΔPA, is given by

$$\Delta PA = H_f°(C_2H_5ONO_2) - H_f°(CH_3ONO_2) +$$
$$H_f°(CH_3OH) - H_f°(C_2H_5OH) + \Delta BE$$

where ΔBE is the difference between the BEs of NO_2^+ to ethanol and to methanol, respectively. In this way, one obtains ΔPA = 1.0 ± 1.2 kcal mol^{-1}. Most of the estimated uncertainty arises from the error bar attached to the heat of formation of CH$_3$ONO$_2$, as large as 1.1 kcal mol^{-1},[29] whereas ΔBE is affected by a relatively small uncertainty, conservatively estimated to be 0.4 kcal mol^{-1}.[22]

The theoretically computed values of the PA of ethyl nitrate and of the $C_2H_5OH-NO_2^+$ BE, 177 ± 2 and 22.0 kcal mol^{-1}, respectively, at 298 K are in satisfactory agreement with the corresponding experimental values. The theoretical study provides an additional and most relevant piece of information, namely, that the local PAs of the alternative proton sites of C_2H_5-ONO_2 are equal.

The thermochemistry of the species and of the processes of interest are illustrated in Figure 3, which utilizes exclusively
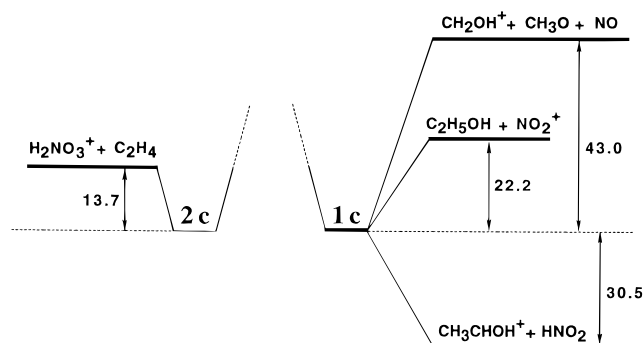
Figure 3. Energy profile of the $(C_2H_5ONO_2)H^+$ protomers and their dissociation processes based on the experimental data from this work and ref 18 and utilizing the theoretically derived notion that **1c** and **2c** have the same stability at 298 K. Energies in kcal mol^{-1}.
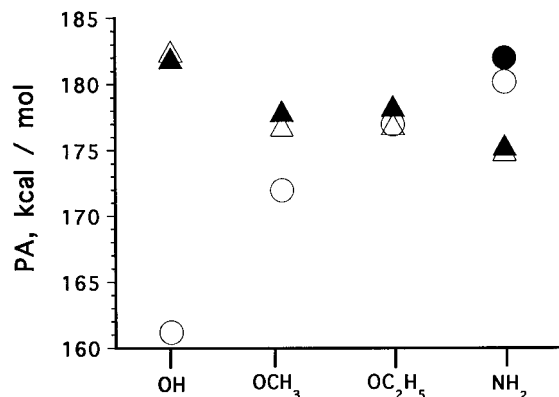

Figure 4. PA of XNO_2 molecules referred to protonation at the X group, yielding protomers **1** (triangles), and at the NO_2 group, yielding protomers **2** (circles). Open and full labels refer to ab initio and experimental data, respectively.

experimental data combined with the theoretically derived notion that protomers **1c** and **2c** have the same stability at 298 K.

The PA Trend along the RONO$_2$ Series. The present results provide additional insight into the long debated problem related to the preferred protonation site and the PA trend of gaseous nitric acid and alkyl nitrates,[11-16,30] as well as of the strictly related nitramide.[31] The overall picture emerging from all relevant data, both experimental and theoretical, available at the present time is illustrated in Figure 4, and its salient features can be outlined as follows.

In the case of $HONO_2$ and CH_3ONO_2 the RO group is the preferred protonation site, namely, ion−molecule complexes of structure **1** are the most stable protomers. In the case of H_2N-NO_2 the NO_2 group is preferred, whereas in the case of C_2H_5-ONO_2 the local PAs of the RO and the NO_2 groups are nearly equal; that is, **1c** and **2c** have the same stability.

As to the stability difference between the isomeric protonated forms of a given molecule, the gap is as large as 20 kcal mol^{-1} in the case of $HONO_2$, decreases to ca. 5 kcal mol^{-1} in the case of CH_3ONO_2, and vanishes in the case of $C_2H_5ONO_2$, to increase again to ca. 7 kcal mol^{-1} in the case of H_2N-NO_2, where the stability order of the protomers is reversed.

Examining the PA trends, a separate discussion of the protonation at the NO_2 group and at the RO or the NH_2 group is in order. In protomers of structure **2**, arising from protonation at NO_2, the latter is covalently bound to the substituent, whose ability to stabilize the positive charge of the $-NOOH^+$ group formed is a key factor in stabilizing the adduct. Consistent with this reasoning, the local PA of the NO_2 group in the molecules of interest is found to increase along the $HO < CH_3O < C_2H_5O < NH_2$ series. Entirely different criteria apply to the protomers

of structure **1**, i.e. ion−molecules complexes characterized by a distant and relatively weak coordination of the monomers, formed upon protonation of the RO or the NH_2 group. In these cases, the charge-stabilizing ability of the RO group is no longer the paramount factor,[32] and as suggested by Lee and Rice,[14] the PA of $RONO_2$ molecules seems to correlate with the difference between the RO−H and RO−NO_2 bond energies. From the results of this study the correlation appears susceptible of extension to R = C_2H_5, based on D_0 values estimated from the heats of formation of the radicals involved.[18,29]

Experimental Section

Materials. All chemicals, including the labeled compounds, were obtained from Aldrich Chemical Co. with a stated purity of 99% or were prepared according to established procedures. The gases were purchased from Matheson Gas Products Inc. and from UCAR Co. with a stated purity in excess of 99.95 mol %.

Mass Spectrometric Measurements. MIKE and CAD spectra were recorded using a ZAB-2F mass spectrometer from VG Micromass Ltd. Typical experimental conditions were as follows: source temperature 150 °C, emission current 0.5 mA, repeller voltage 0 V, accelerating voltage 8 kV. The MIKE spectra of the nitronium-bound dimers were recorded maintaining a source temperature of 40−50 °C, by a specially built cooling system utilizing a stream of cold N_2. The CAD spectra represent the sum of at least 40 scans acquired with an energy resolution of 4000 fwhm. Helium, used as the collision gas, was admitted into the cell adjusting its pressure to the value required to achieve a reduction of the main beam intensity, to ca. 30% of its original value. The ICR experiments were performed using a Bruker Spectrospin Apex 47 FT-ICR mass spectrometer, equipped with an external CI source, two pulsed valves, and a XMASS-TM data system. The ions formed in the external source were driven into the cell and allowed to equilibrate with a gaseous mixture prepared from weighted amounts of the two ligands of interest. When required, the ions were thermalized by introducing Ar via the pulsed valves.[20]

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