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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Received: May 7, 1996; In Final Form: June 20, 1996[®]

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 $C_2H_5^-$ ONO₂. The BE of NO₂⁺ 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 $2c \rightarrow 1c$ isomerization is characterized by a ΔG° 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 NO₂ 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 RONO₂ homologous series. It is shown that entirely different factors control the local PA of the RO and the NO₂ 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**,

$$(\text{ROHNO}_2)^+$$

$$\mathbf{a} \ \mathbf{R} = \mathbf{H}, \ \mathbf{b} \ \mathbf{R} = \mathbf{CH}_3, \ \mathbf{c} \ \mathbf{R} = \mathbf{C}_2\mathbf{H}_5$$

$$(\text{RONO}_2)\mathbf{H}^+$$

$$\mathbf{a} \ \mathbf{R} = \mathbf{H}, \ \mathbf{b} \ \mathbf{R} = \mathbf{CH}_3, \ \mathbf{c} \ \mathbf{R} = \mathbf{C}_2\mathbf{H}_5$$

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 \pm 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 \pm 2.3 and 175.0 \pm 2.5 kcal mol⁻¹ to HNO₃ and CH₃ONO₂, respectively,¹⁵ and the corresponding values from Fourier-transform ion cyclotron resonance (FT-ICR) experiments are 182.0 \pm 2.3¹⁶ and 178.0 \pm 2.0 kcal mol⁻¹.¹⁷ The larger PA of HNO₃ than of CH₃ONO₂ can be regarded as firmly established, since the experimental

study of the ligand-exchange equilibrium in the H₂O/NO₂^{+/} MeOH system gave a ΔPA value of 4.0 \pm 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 RONO₂ homologues to verify whether the observed trend holds for alkyl groups, such as C₂H₅, characterized by a better σ -donating ability than H and CH₃. 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 $R = C_2H_5$. 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 C₂H₅ONO₂ 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" technique¹⁸ 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,

$$AH^{+} + C_{2}H_{5}ONO_{2} \rightarrow A + (C_{2}H_{5}ONO_{2})H^{+}$$
(1)

whose structure is expected to correspond exclusively to that of isomer **1**, obtained from ligand-exchange reactions where L denotes a suitable nucleophile.

$$LNO_{2}^{+} + C_{2}H_{5}OH \rightarrow L + (C_{2}H_{5}OH - NO_{2})^{+}$$
 (2)

S0022-3654(96)01323-8 CCC: \$12.00 © 1996 American Chemical Society

[®] Abstract published in Advance ACS Abstracts, September 1, 1996.

TABLE 1: MIKE Spectra of (C₂H₅ONO₂)H⁺ Ions from Different Reactions

		% intensity ^a						
		reaction 2						
m/z	$C_n H_5^+ (n = 1, 2)$	i-C ₃ H ₇ +	H_3O^+	$C_2H_5ONO_2^{\bullet+}$	CH ₃ OHNO ₂ ⁺ , CH ₃ ONO ₂ NO 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 (C₂H₅ONO₂)- H^+ population have been changed by using acids, i.e. $C_nH_5^+$ (n = 1, 2), H₃O⁺, and *i*-C₃H₇⁺, 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 selfprotonation process occurring in C2H5ONO2/CI is unknown. However, owing to the relatively high pressure (>0.2 Torr) of neutral ethyl nitrate, the (C₂H₅ONO₂)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 H₂NO₃⁺ 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 (C₂H₅ONO₂)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 ₂ H ₅ ONO ₂)H ⁺	Ions from
Different Re	eactions		

	% intensity ^a						
		reaction 2					
m/z	$\frac{\mathrm{C}_{n}\mathrm{H}_{5}^{+}}{(n=1,2)}$	<i>i</i> -C ₃ H ₇ ⁺	${ m H_3O^+}$	C ₂ H ₅ ONO ₂ •+	CH ₃ OHNO ₂ ⁺ , CH ₃ ONO ₂ NO 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		
/0	1.5	1.5	1.5	2.2	1.5		

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

 $C_2H_5O^+$, 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 HNO₂ 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 CH₃CDOH⁺ fragment of m/z = 46, isobaric with NO₂⁺, from the adduct **1c** obtained upon addition of NO₂⁺ to CH₃CD₂OH. The mixed **1c/2c** population from the protonation of C₂H₅ONO₂ with H₃O⁺ displays a CH₃CHOH⁺ fragment of m/z = 45, which disappears if D₃O⁺ is used instead of H₃O⁺. This can be rationalized assuming that in the case of deuteronation a CH₃CHOD⁺ fragment is formed, which again happens to be isobaric with the NO₂⁺ ions, a major peak in the CAD spectrum. The above observations strongly suggest that the fragment of m/z = 45from (CH₃CH₂ONO₂)H⁺ has the CH₃CHOH⁺ 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 ¹³C- 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 (C₂H₅ONO₂)D⁺ precursor.

CH₃O⁺, m/z = 31. The m/z ratio increases to 32 when the parent contains two ¹³C atoms, and the same mass shift is observed in the fragment from the (CH₃CH₂ONO₂)D⁺ precursor. The H atoms of the CH₃O⁺ 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 CD₃CH₂OHNO₂⁺.

MIKE Spectra of NO₂⁺ **Bound Dimers.** The spectra of the adducts obtained by CI of suitable L_1/L_2 ligand pairs using NO₂ or CH₃ONO₂ as a reactant gas are reported in Table 3.

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



Figure 1. (a) Time profile of the ionic intensities in the reaction of $(C_2H_5ONO_2)H^+$, m/z = 92, with CH₃NO₂, yielding NO₂⁺, m/z = 46, $(CH_3NO_2)H^+$, m/z = 62, and $(CH_3NO_2)NO_2^+$, m/z = 107. (b) Same, after thermalization of (C₂H₅ONO₂)H⁺ ions (see text).

Certain adducts, e.g. in the case of the CH₃NO₂/C₂H₅OH pair, give only $L_1 NO_2^+$ metastable fragments, whereas in other systems the dissociation of the adducts gives, in addition, fragments corresponding to protonated ligands. Application of the kinetic method²¹ and the calibration reported in an extensive study on NO₂⁺ bound dimers²² lead to a ΔG° difference of 0.7 \pm 0.1 and 1.7 \pm 0.1 kcal mol⁻¹ for the CH₃NO₂/C₂H₅OH and the C₂H₅NO₂/C₂H₅OH pairs, respectively. Under the usual assumption that $\delta(\Delta G^{\circ}) \simeq \delta(\Delta H^{\circ})$ and utilizing the available NO2⁺ BE scale,²² one arrives at a NO2⁺ BE of C2H5OH of 22.1 and 22.3 kcal mol⁻¹ from the dissociation of CH₃NO₂- $(NO_2^+)C_2H_5OH$ 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 NO₂⁺ BE of C₂H₅OH 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

fragments (m/z) , I%						
$\begin{array}{l} H_3NO_2NO_2^+ \left(107\right) = 82.6\% \\ H_3NO_2NO_2^+ \left(107\right) = 82.7\% \\ H_3NO_2H^+ \left(62\right) = 1.9\% \\ D_3NO_2H^+ \left(65\right) = 0.9\% \\ 2H_5NO_2H^+ \left(76\right) = 23.2\% \\ 2H_5NO_2D^+ \left(77\right) = 27.9\% \\ 2H_5NO_2H^+ \left(76\right) = 31.1\% \end{array}$	$\begin{array}{l} C_2H_5OHNO_2^+ (92) = 17.4\% \\ C_2D_5ODNO_2^+ (98) = 17.3\% \\ (C_2H_5ONO_2)H^+ (92) = 17.8\% \\ (C_2H_5ONO_2)H^+ (92) = 17.7\% \\ C_2H_5OHNO_2^+ (92) = 2.0\% \\ C_2D_5ODNO_2^+ (98) = 3.9\% \\ (C_2H_5ONO_2)H^+ (92) = 1.0\% \end{array}$	$CH_{3}NO_{2}NO_{2}^{+}(107) = 80.3\%$ $CD_{3}NO_{2}NO_{2}^{+}(110) = 81.4\%$ $C_{2}H_{5}NO_{2}NO_{2}^{+}(121) = 74.8\%$ $C_{2}H_{5}NO_{2}NO_{2}^{+}(121) = 68.2$ $C_{2}H_{5}NO_{2}NO_{2}^{+}(121) = 67.9\%$				

with CH₃NO₂ 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 NO₂⁺ transfer to CH₃NO₂, whereas H⁺ transfer is depressed and dissociation into NO₂⁺ 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 (CH₃ONO₂)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 $2c \rightarrow 1c$ conversion.

Application of the FT-ICR Equilibrium Method. CH₃O- $(NO_2)_2^+$ ions, produced by CH₃ONO₂/CI in the external ion source, were introduced into the resonance cell containing C₂H₅OH/C₂H₅NO₂ mixtures of known composition. The nitrated adducts formed via NO₂⁺ transfer from CH₃O(NO₂)₂⁺ to both ligands were allowed to equilibrate according to the ligand-exchange reaction

$$C_{2}H_{5}OHNO_{2}^{+} + C_{2}H_{5}NO_{2} \rightleftharpoons$$
$$m/z = 92$$
$$C_{2}H_{5}OH + C_{2}H_{5}NO_{2}NO_{2}^{+} (3)$$
$$m/z = 121$$

Owing to the occurrence of the competitive process

$$C_{2}H_{5}OHNO_{2}^{+} + C_{2}H_{5}NO_{2} \rightarrow C_{2}H_{5}ONO_{2} + (C_{2}H_{5}NO_{2})H^{+}$$
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

$$K_3 = \frac{K_{\rm app}}{1 - k_4 i_{92} / k_3 i_{122}}$$

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 cm³ 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 cm³ molecule⁻¹ s⁻¹. From these values and the i_{92}/i_{121} ratios



1c

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 NO₂⁺ BE to C₂H₅NO₂, and under the customary assumption that $\Delta G_3^{\circ} \cong \Delta H_3^{\circ}$, one obtains a BE value of ca. 22 kcal mol⁻¹ for the C₂H₅OHNO₂⁺ complex **1c**, in excellent agreement with the 22.2 \pm 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 highlevel 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 fourthorder, 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)/6-311G(d,p)] + E[MP2/6-311+G(3df,2p) - E[MP2/6-311G(d,p) + ZPE[HF/6-31G(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		$E_{\text{G2MP2}}(0 \text{ K})$	<i>H</i> _{G2MP2} (298 K)
$\begin{array}{c} C_{2}H_{5}ONO_{2} \\ C_{2}H_{5}OHNO_{2}^{+}(1) \\ C_{2}H_{5}ONO_{2}H^{+}(2) \\ C_{2}H_{5}OH \\ NO_{2}^{+} \end{array}$	$C_{\rm s}$ $C_{\rm s}$ $C_{\rm s}$ Dooh	$\begin{array}{r} -358.994\ 27\\ -359.275\ 72\\ -359.274\ 46\\ -154.760\ 51\\ -204.479\ 865\end{array}$	$\begin{array}{r} -358.987\ 095\\ -359.266\ 645\\ -359.266\ 825\\ -154.755\ 20\\ -204.476\ 305\end{array}$

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 formulas²⁶ 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 $0.8 \text{ kcal mol}^{-1}$. 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 $2c \rightarrow 1c$ isomerization is found to be -3 kcal mol-1 at 298 K, showing that the process is marginally exoergonic.

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 NO₂⁺, ethanol, and **1c**, we obtain a C₂H₅-OH–NO₂⁺ 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 (C₂H₅-ONO₂)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 ¹³C and d-labeled species, provides convincing evidence for the existence of two isomers. Model ions **1c** display a dissociation pattern dominated by the NO₂⁺ fragment, m/z = 46, i.e. the ligand loss typical of an ion-molecule complex. Another significant process leads to formation of the

$$CH_{3} - CH_{+}^{+} \xrightarrow{H}_{-O}^{+} NO \longrightarrow CH_{3}CHOH^{+} + HNO_{2}$$
(5)

 $C_2H_5O^+$ 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.

$$H_{3}C \xrightarrow{CH_{2}} H_{1}C \xrightarrow{H_{2}} CH_{2}OH^{+} + CH_{3}ONO$$
(6)

The only, conspicuous feature of isomer 2c is the fragmentation into $H_2NO_3^+$, 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}

$$\begin{array}{cccc} H_{2} & H_{2} & H_{2} \\ H_{2} & H_{2$$

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 (H₂NO₃⁺) and 29 (protonated ethylene) follow parallel trends, suggesting that both originate from **2c**, whereas NO₂⁺, 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	$\frac{\mathrm{C}_{n}\mathrm{H}_{5}^{+}}{(n=1,2)}$	<i>i</i> -C ₃ H ₇ +	H_3O^+	C ₂ H ₅ ONO ₂ •+	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 $(C_2H_5ONO)H^+$ ions from reaction 1 performed with $C_nH_5^+$ ions.

facilitate comparison, the ratios typical of the ions from the protonation by $C_nH_5^+$ 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: selfprotonation < protonation by $H_3O^+ <$ protonation by *i*-C₃H₇⁺ < protonation by $C_nH_5^+$. 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 $C_2H_5ONO_2$ by *i*- $C_3H_7^+$ than from the appreciably exothermic (some 10 kcal mol⁻¹) protonation by H_3O^+ . 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 C₂H₅ONO₂/CI, where the initially formed 2c isomer undergoes the intermolecular isomerization

$$C_{2}H_{5}ONO_{2}H^{+} + C_{2}H_{5}ONO_{2} \rightarrow 2c$$

$$C_{2}H_{5}ONO_{2} + (C_{2}H_{5}OHNO_{2})^{+} (8)$$
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-

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

frequencies		IR intensities	frequencies		IR intensities		
(cm^{-1})	symmetry	(km/mol)	(cm^{-1})	symmetry	(km/mol)		
CaHeONOa							
108.9	Α″	0.9	1419.3	Α″	1.3		
131.5	Α″	0.9	1519.0	A'	138.4		
274.6	Α″	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'	26	1642.4	A'	82		
890.2	Δ"	51	1672.2	Δ'	2.4		
917.8	Δ"	29.2	1906.0	Δ'	722.5		
1003.0	Δ'	62	3224.4	Δ'	16.2		
1102.0	A'	15.2	2284.0	A'	1.2		
1187 /	Λ \	263.0	3204.0	Λ \	34.7		
1252.7	Λ \	24.3	2201 5	Λ \/''	10.0		
1206.9	A ^"	24.3	2240.2	A ^"	20.0		
1290.8	A	0.2	5549.5	A	30.9		
		C_2H_5O	HNO_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	Α″	18.9		
1135.5	A'	81.7	3301.0	A'	13.8		
1172.4	A'	23.7	3302.5	Α″	51.1		
1291.5	Α″	7.3	4081.1	A'	107.7		
		CUO	NO II ⁺				
88 A	۸."	$C_2H_5O_2$	NO ₂ H ⁺ 1291.5	۸′	610.9		
140.7	A \/''	0.1	1208.0	A \/''	019.8		
216.1	A ^″	2.0	1524.9	A ^'	4.4		
210.1	A ^″	2.0	1534.6	A A'	21.4		
2/1.1	A A'	1.5	15/2.7	A ^"	10.8		
578.8	A A'	30.9	1613.2	A A'	14.1		
525.2	A	/4.9	1633.8	A	3.0		
568.7	A	183.4	1634.9	A	14.5		
/53.8	A'	1.4	16/9./	A	/8.0		
8/0.0	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	Α"	10.7	3884.3	A'	383.3		

metric evidence suggests that intramolecular $2c \rightarrow 1c$ 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 C2H5-ONO₂, suggesting that the available literature data should be taken with reservation.²⁸ Under the circumstances, an indirect approach utilizing the NO₂⁺ BE to C₂H₅OH appears the least unsatisfactory. By combining the BE from the kinetic and the equilibrium method, 22.2 \pm 2.6 kcal mol⁻¹, with the heats of formation of H⁺, NO₂⁺, C₂H₅OH, and C₂H₅ONO₂, one obtains $PA(C_2H_5ONO_2) = 178.4 \pm 2.6 \text{ kcal mol}^{-1}$. Such large error bars and the correspondingly high uncertainty of the PA of CH₃- ONO_2 , 178 \pm 2 kcal mol⁻¹, make it difficult to ascertain the PA trends of homologous RONO₂ 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

$$\Delta PA = H_{f}^{\circ}(C_{2}H_{5}ONO_{2}) - H_{f}^{\circ}(CH_{3}ONO_{2}) + H_{f}^{\circ}(CH_{3}OH) - H_{f}^{\circ}(C_{2}H_{5}OH) + \Delta BE$$

where ΔBE is the difference between the BEs of NO₂⁺ to ethanol and to methanol, respectively. In this way, one obtains $\Delta PA = 1.0 \pm 1.2$ kcal mol⁻¹. Most of the estimated uncertainty arises from the error bar attached to the heat of formation of CH₃ONO₂, 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 C₂H₅OH–NO₂⁺ 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 C₂H₅-ONO₂ 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 XNO₂ molecules referred to protonation at the X group, yielding protomers 1 (triangles), and at the NO₂ 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 RONO₂ 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 HONO₂ and CH₃ONO₂ the RO group is the preferred protonation site, namely, ion-molecule complexes of structure **1** are the most stable protomers. In the case of H₂N-NO₂ the NO₂ group is preferred, whereas in the case of C₂H₅-ONO₂ the local PAs of the RO and the NO₂ 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 HONO₂, decreases to ca. 5 kcal mol⁻¹ in the case of CH₃ONO₂, and vanishes in the case of C₂H₅ONO₂, to increase again to ca. 7 kcal mol⁻¹ in the case of H₂N–NO₂, where the stability order of the protomers is reversed.

Examining the PA trends, a separate discussion of the protonation at the NO₂ group and at the RO or the NH₂ group is in order. In protomers of structure **2**, arising from protonation at NO₂, 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 NO₂ group in the molecules of interest is found to increase along the HO < CH₃O < C₂H₅O < NH₂ 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 NH₂ 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 RONO₂ molecules seems to correlate with the difference between the RO-H and RO-NO₂ 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 N2. 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

Acknowledgment. We thank F. Grandinetti for his invaluable help and many useful discussions and F. Angelelli for FT-ICR measurements. The financial support of the Rome University "La Sapienza" and the Italian National Research Council (CNR) is gratefully acknowledged.

References and Notes

- (1) Fehsenfeld, F. C.; Ferguson, E. E. J. Geoph. Res. 1969, 74, 2217.
- (2) Linenberger, W. C.; Puckett, L. J. Phys. Res. 1969, 187, 286.
- (3) Ferguson, E. E.; Fehsenfeld, F. C.; Albritton, L. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. I, Chapter 2.

(4) Zhang, X.; Mereand, E. L.; Castleman, A. W., Jr. J. Phys. Chem. 1994, 98, 3554.

(5) Cao, Y.; Choi, J.-H.; Haas, B.-M.; Okamura, M. J. Phys. Chem. 1994, 98, 12176.

(6) Attinà, M.; Cacace, F.; Yañez, M. J. Am. Chem. Soc. 1987, 109, 5092.

(7) Attinà, M.; Cacace, F.; de Petris, G. Angew. Chem., Int. Ed. Engl. 1987, 26, 1177.

(8) Attinà, M.; Cacace, F. Gazz. Chim. Ital. 1989, 118, 241.

(9) Szabò, K. J.; Hörnfeld, A. B.; Gronowitz, S. J. Am. Chem. Soc. 1992, 114, 6827.

(10) Aschi, M.; Attinà, M.; Cacace, F.; Ricci, A. J. Am. Chem. Soc. 1994, 116, 9535.

(11) Cacace, F.; Attinà, M.; de Petris, G.; Speranza, M. J. Am. Chem. Soc. 1990, 112, 1014.

- (12) de Petris, G. Org. Mass Spectrom. 1990, 25, 83.
- (13) Lee, T. J.; Rice, J. E. J. Phys. Chem. 1992, 96, 650.
- (14) Lee, T. J.; Rice, J. E. J. Am. Chem. Soc. 1992, 114, 8247.
- (15) Sunderlin, L. S.; Squires, R. R. Chem. Phys. Lett. 1993, 212, 307.

(16) Cacace, F.; Attinà, M.; de Petris, G.; Speranza, M. J. Am. Chem. Soc. 1994, 116, 6413.

(17) Ricci, A. Org. Mass Spectrom. 1994, 29, 53. All PA values are referred to 298 K.

(18) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin,

- R. D.; Mallard, W. G. J. Phys. Chem. Ref. Data 1988, 17, Suppl. 1, 16.
- (19) Kriemler, P.; Buttrill, S. E., Jr. J. Am. Chem. Soc. 1970, 92, 1123.
 (20) Thölmann, D.; Grützmacher, H. Fr.-ICR Ion Trap. Newslett. 1992, 25, 17.
- (21) Cooks, G. R.; Patrick, J. S.; Kotiaho, T.; McLukey, S. A. Mass Spectrom. Rev. 1994, 13, 287.

(22) A nitronium ion affinity scale has been reported by the following: Cacace, F.; de Petris, G.; Pepi, F.; Angelelli, F. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 8635.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Chreseman, J. R.; Keith, T. A.; Petersson, G. A.; Zakrzweski, V. G.; Ortiz, G. V.; Foresman, J. B.; Cioslowki, J.; Stefanov, B. B.; Nanaykkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Reploge, E. S. A.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, O. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94* (Revision C.2); Gaussian, Inc.: Pittsburgh, PA, 1995. (24) Curtiss, L. A.; Ragavachari, R.; Pople, J. A. J. Chem. Phys. 1993, 98, 1293.

(25) Smith, B. J.; Radom, L. Chem. Phys. Lett. 1994, 231, 345.

(26) McQuarrie, D. Statistical Mechanics; Harper and Row: New York, 1976.

- (27) Büker, H.; Grützmacher, H.-F. Int. J. Mass Spectrom. Ion Processes 1991, 109, 95.
- (28) Early ICR bracketing experiments, ref 19, gave a PA of C₂H₅ONO₂
- of 180 ± 3 kcal mol⁻¹, which, adjusted to the recent scale by Szulejko, J.
- E.; McMahon, T. B. J. Am. Chem. Soc. **1993**, 115, 7839, amounts to 177.4 \pm 3 kcal mol⁻¹. Recent FT-ICR bracketing experiments gave a PA of 181.7
- ± 2 kcal mol⁻¹, ref 11. (29) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of*

Organic Compounds, 2nd ed.; Chapman & Hall: London, 1986.

(30) Nguyen, M.-T.; Hegarty, A. F. J. Chem. Soc., Perkin Trans. 2 1984, 2043.

(31) Attinà, M.; Cacace, F.; Ciliberto, E.; de Petris, G.; Grandinetti, F.; Pepi, F.; Ricci, A. J. Am. Chem. Soc. **1993**, 115, 12398.

(32) The trend is not general for all RXH⁺ ion-molecule complexes. However, recent results from this laboratory indicate that it holds for RONO molecules as well.

JP961323D