J. Am. Chem. Soc. 1994, 116, 6413–6417 6413

Is the Proton Affinity of Nitric Acid Larger Than the Proton Affinity of Methyl Nitrate? A Direct Experimental Answer

Fulvio Cacace,[*,†] **Marina Attinà,**[†] **Giulia de Petris,**[‡] **and Maurizio Speranza**[†]

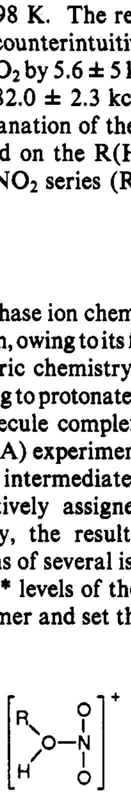
Contribution from the Università di Roma "La Sapienza", P. le A. Moro 5, 00185 Rome, Italy, and Università della Tuscia, Via S. C. De Lellis, 01100 Viterbo, Italy

Received November 1, 1993. Revised Manuscript Received March 28, 1994[●]

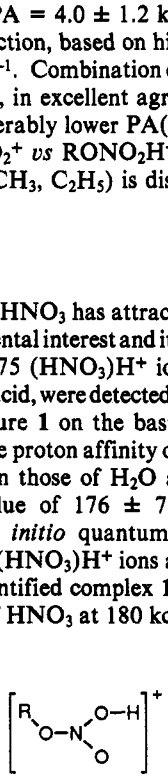
Abstract: A direct experimental approach based on the evaluation of the ligand exchange equilibrium $H_2O\text{-}NO_2^+ + CH_3OH \rightleftharpoons CH_3(H)O\text{-}NO_2^+ + H_2O$ has been exploited for the determination of $\Delta PA = PA(HNO_3) - PA(CH_3ONO_2)$ at 298 K. The result, $\Delta PA = 4.0 \pm 1.2$ kcal mol^{-1}, is sufficiently accurate to provide firm experimental support to the counterintuitive prediction, based on high-level *ab initio* calculations, that the PA of HNO_3 *exceeds* that of CH_3ONO_2 by 5.6 ± 5 kcal mol^{-1}. Combination of the experimental ΔPA with the known PA of CH_3ONO_2 gives $PA(HNO_3) = 182.0 \pm 2.3$ kcal mol^{-1}, in excellent agreement with the theoretically computed value, 182.5 ± 3 kcal mol^{-1}. An explanation of the considerably lower $PA(HNO_3)$ value derived from earlier ICR bracketing experiments is offered, based on the $R(H)O\text{-}NO_2^+$ *vs* $RONO_2H^+$ isomerism, whose role in determining the observed PA trend along the $RONO_2$ series ($R = H, CH_3, C_2H_5$) is discussed.

Introduction

The gas-phase ion chemistry of HNO_3 has attracted considerable attention, owing to its fundamental interest and its importance in atmospheric chemistry. In 1975 $(HNO_3)H^+$ ions, formally corresponding to protonated nitric acid, were detected and assigned the ion–molecule complex structure **1** on the basis of flowing afterglow (FA) experiments.[1] The proton affinity of HNO_3 was found to be intermediate between those of H_2O and of NH_3, being tentatively assigned a value of 176 ± 7 kcal mol^{-1}. Subsequently, the results of *ab initio* quantum mechanical investigations of several isomeric $(HNO_3)H^+$ ions at the 4–31G and 6–31G** levels of theory identified complex **1** as the most stable protomer and set the PA of HNO_3 at 180 kcal mol^{-1} at 0 K.[2]



1, R = H
2, R = CH_3
3, R = C_2H_5



4, R = H
5, R = CH_3
6, R = C_2H_5

In 1989 the experimental characterization of protomer **4**, and hence the demonstration that two distinct $(HNO_3)H^+$ isomers actually exist in the gas phase, was achieved as a result of the comparative analysis by mass-analyzed ion kinetic energy (MIKE) and collisionally activated dissociation (CAD) spectrometry of $(HNO_3)H^+$ populations from different reactions. The results showed that rearrangement of **4** into the more stable protomer **1** requires overcoming a high activation barrier, which accounts for the long lifetime ($\geq 10^{-5}$ s) of the ion.[3,4] Direct evaluation of the PA of HNO_3 by the accurate method based on ion cyclotron resonance (ICR) equilibrium measurements[5] was prevented by the tendency of **1** to dissociate into H_2O and NO_2^+ under typical ICR conditions and to undergo predominant transfer of NO_2^+, rather than of H^+, to the reference bases used. These problems, and the complication arising from the existence of two $(HNO_3)H^+$ isomers, made it necessary to resort to the ICR bracketing technique, whose result, $PA(HNO_3) = 168 \pm 3$ kcal mol^{-1},[4] although less reliable,[5] was nevertheless regarded as reasonably accurate, being apparently consistent with the PA of the strictly related CH_3ONO_2 molecule. Protonation of the latter was also found to give two isomeric ions, **2** and **5**, the ion–molecule complex **2** being experimentally characterized as the most stable one, in complete analogy with the HNO_3 system.[6,7] Based on the ICR equilibrium measurements, the PA of CH_3ONO_2, referred to the formation of **2**, was estimated to be 176 ± 2 kcal mol^{-1}.[8] Since the PA of a HO-X molecule is generally *lower* than that of the corresponding CH_3O-X molecule by 8-15 kcal mol^{-1},[5] the estimated PA of HNO_3 was seemingly consistent with the PA of CH_3ONO_2, higher by 8 kcal mol^{-1}.

Lee and Rice have recently investigated several protonated forms of HNO_3, confirming complex **1** as the most stable protomer and estimating that ions of structure **4** are less stable by some 20 kcal mol^{-1}.[9] Whereas these conclusions are fully consistent with the experimental results, the PA of HNO_3 computed with the CCSD(T) method amounts to 182.5 ± 3 kcal mol^{-1} at 298 K, considerably higher than the 168 ± 3 value estimated from the bracketing experiments. Even more significantly, in a subsequent theoretical study Lee and Rice[10] reported that the PA of CH_3ONO_2, 176.9 ± 5 kcal mol^{-1}, is *lower* than that of HNO_3.

The theoretically established basicity trend obviously deserves accurate experimental verification because, in such a particularly

---

[†] Università di Roma "La Sapienza".
[‡] Università della Tuscia.
[●] Abstract published in *Advance ACS Abstracts*, June 15, 1994.

(1) Fehsenfeld, F. C.; Howard, C. J.; Schmeltekopf, A. L. *J. Chem. Phys.* **1975**, *63*, 2835.

(2) Nguyen, M.-T.; Hegarty, A. F. *J. Chem. Soc. Perkin Trans. 2* **1984**, 2043. Note that in mass spectrometric reports the term "structure" is used simply to denote the connectivity of the ions, whereas theoretical approaches give far more detailed information, *e.g.* the bond lengths and angles, the characterization of conformers, etc.

(3) Cacace, F.; Attinà, M.; de Petris, G.; Speranza, M. *J. Am. Chem. Soc.* **1989**, *111*, 5481.

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

(5) For a discussion of the experimental methods for the determination of gas-phase PA, cf.: (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R.D.; Mallard, W. G. *J. Chem. Phys. Ref. Data* **1988**, *17* Suppl.1 and references therein. This compilation has also been used as a source of thermochemical data unless otherwise stated. The $\Delta H_f°$ of NO_2^+ at 298 K has been corrected, consistent with the revised IP of NO_2. Cf.: (b) Clemmer, D.E.; Armentrout, P. B. *J. Chem. Phys.* **1992**, *97*, 2451.

(6) de Petris, G. *Org. Mass Spectrom.* **1990**, *25*, 83.

(7) The $(CH_3ONO_2)H^+$ isomers have been investigated as well by *ab initio* methods at the 4–31G level of theory. Cf.: Bernardi, F.; Cacace, F.; Grandinetti, F. *J. Chem. Soc. Perkin Trans. 2* **1989**, 413.

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

(9) Lee, T. J.; Rice, J. E. *J.Phys.Chem.* **1992**, *96*, 650.

(10) Lee, T. J.; Rice, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 8247.

simple and important system, it runs contrary to common chemical intuition and represents a conspicuous exception to the general observation that PA(CH_3O-X) > PA(HO-X). Furthermore, the difference between the PA of HNO_3 and of CH_3ONO_2, theoretically computed by Lee and Rice, $\Delta PA = 5.6$ kcal mol^{-1}, is affected by a large uncertainty, ±5 kcal mol^{-1} .[9,10]

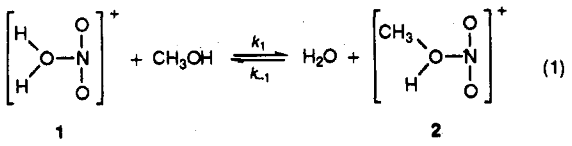
The first experimental response elicited by these counterintuitive theoretical results is the measurement of the binding energy (BE) of H_2O and CH_3OH to NO_2^+, performed by Sunderlin and Squires by energy-resolved CAD in a FA-triple quadrupole apparatus.[11] From the heats of formation of the ions **1** and **2** obtained in this way, combined with those of H^+, HNO_3, and CH_3ONO_2, they obtained $\Delta PA = 2.7 \pm 3.4$ kcal mol^{-1}, in qualitative agreement with the theoretically predicted trend. This result, however, can hardly be regarded as conclusive, since its cumulative uncertainty exceeds the small quantity being evaluated, and the PA of HNO_3 obtained differs considerably (4.8 kcal mol^{-1}) from the theoretically calculated value.[9]

In view of the relevance of the problem, we have decided to reevaluate the *difference* between the PA of HNO_3 and CH_3ONO_2 by a direct experimental approach of adequate accuracy.

Methodology

Critical examination of the conceivable experimental approaches leads to the conclusion that the accuracy of the ΔPA evaluation can hardly be improved over that achieved by Sunderlin and Squires[11] *if the PAs of HNO_3 and of CH_3ONO_2 are measured separately*. The significant improvement required for meaningful comparison with, and quantitative verification of, the theoretically computed ΔPA value can only be expected from an experiment designed for *direct* correlation of the PAs of the species of interest.

To this end, a FT-ICR study has been undertaken, based on the evaluation of the equilibrium constant of the reaction in view



of the following valuable features: first, process 1 involves NO_2^+ transfer, which predominates over deprotonation of **1** and **2** by gaseous bases. In this way the higher rate of NO_2^+ than of H^+ transfer, which represents a serious problem in the evaluation of prototropic equilibria, turns into a valuable asset. In the second place, the very nature of reaction (1), a simple ligand exchange, ensures that only **1** and **2**, the most stable protomers, are involved in the equilibrium, which is far less certain when the ions are obtained from the protonation of HNO_3 and CH_3ONO_2. $\Delta H_1°$ corresponds to the difference of the BE of CH_3OH and H_2O to NO_2^+, and its evaluation allows one to calculate $\Delta H_f°$ (**1**) − $\Delta H_f°$ (**2**), which in turn can be utilized to obtain ΔPA.

Results

Evaluation of $\Delta G_1°$. Reaction (1) has been studied by FT-ICR mass spectrometry at 298 K, approaching equilibrium from both sides. To this end, $(HNO_3)H^+$ or $(CH_3ONO_2)H^+$ ions produced in the external CI source of the spectrometer were introduced into the resonance cell containing H_2O/CH_3OH mixtures of different composition, characterized by a $[H_2O]$:$[CH_3OH]$ ratio ranging from 30:1 to 50:1 at total pressures of (1–5) × 10^{-7} Torr. Care was taken to correct the readings of the ionization gauge for its response to H_2O, using to this end known rate constants of suitable ion–molecule reactions.[12] The ions were allowed to interact with the neutrals for sufficiently long time (up to 5–10 s) to allow their collisional cooling and the removal of any protomers **4** or **5** present in the initial ionic populations. The effectiveness of this procedure is demonstrated by control experiments based on the reactions of **1** and **2** with $H_2{}^{18}O$ and $CH_3{}^{18}OH$, respectively. The relevant results show that the surviving ions incorporate only one ^{18}O atom, pointing to the occurrence of ligand exchange processes, $H_2{}^{18}O$ for H_2O and $CH_3{}^{18}OH$ for CH_3OH, which are accessible exclusively to ion-molecule complexes of structures **1** and **2**. Following the cooling period, ions **1** or **2** were isolated by ejecting all other charged species and allowed to equilibrate with the H_2O/CH_3OH mixture. Typical plots of the ionic abundances as a function of the reaction time are illustrated in Figures 1 and 2. It is apparent that after an initial equilibration period the [**1**]:[**2**] ratio reaches a constant value, which however reflects a steady-state condition, rather than a true equilibrium, owing to the incursion of the reactions

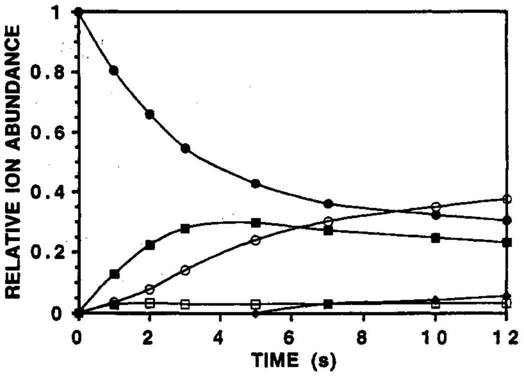


Figure 1. Time dependence of the relative abundances of the charged species following introduction of ions **1** into a 30:1 H_2O/CH_3OH gaseous mixture at 298 K and a total pressure of 2.1 × 10^{-7} Torr: (●) **1**; (■) **2**; (○) $CH_3OH_2^+$; (□) NO_2^+; (◆) $(CH_3)_2OH^+$.

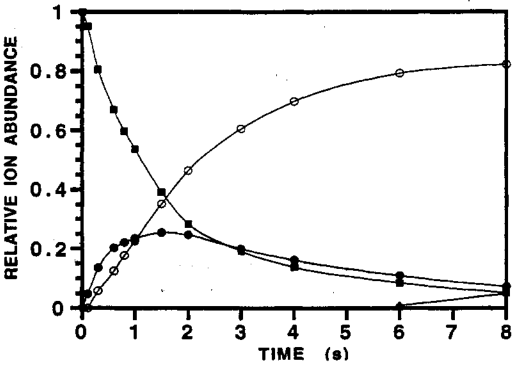


Figure 2. Time dependence of the relative abundances of the charged species following introduction of ions **2** into a 50:1 H_2O/CH_3OH gaseous mixture at 298 K and a total pressure of 2.6 × 10^{-7} Torr. Labels are as in Figure 1.

$$1 + CH_3OH \xrightarrow{k_2} HNO_3 + CH_3OH_2^+ \qquad (2)$$

$$2 + CH_3OH \xrightarrow{k_3} CH_3ONO_2 + CH_3OH_2^+ \qquad (3)$$

whose product, $CH_3OH_2^+$, becomes predominant at long reaction times. For most purposes the apparent equilibrium constant K_{app} deduced from the steady-state abundance ratio of ions **1** and **2** is sufficiently close to the true equilibrium constant K_1 to be used directly in the calculation of $\Delta G_1°$.

However, in view of the accuracy required by the specific purposes of this work, the true equilibrium constant has been evaluated by applying the steady-state approximation to the set of reactions (1), (2) and (3). In this way one arrives at the

---

(11) Sunderlin, L. S.; Squires, R. R. *Chem.Phys.Lett.* **1993**, *212*, 307.

(12) (a) Kebarle, P. In *Ion-Molecule Reactions*; Franklin, J. L., Ed.; Butterworths: London, 1972; Vol. 1 p. 330. (b) Ryan, K. R. *J. Chem. Phys.* **1970**, *52*, 6009. (c) Bartmess, J. E. *Vacuum* **1983**, *33*, 149.

expression

$$K_1 = \frac{K_{app} + k_3[\mathbf{2}]/2k_{-1}[\mathbf{1}]}{1 + k_2/2k_1}$$

where the concentration ratio is that measured under steady-state conditions.

In each of the many experiments performed at 298 K using different H_2O/CH_3OH ratios, K_{app} has been evaluated from the relative abundances of **1** and **2** measured under steady-state conditions, whereas the initial-rate method has been used to evaluate the required k_1, k_{-1}, k_2, and k_3 values. The latter ones are affected by large uncertainties and change appreciably in the different experiments, typical ranges being $k_1 = (6.6–13.9) \times 10^{-10}$, $k_{-1} = (4.3–5.2) \times 10^{-11}$, $k_2 = (2.5–10.4) \times 10^{-10}$, and $k_3 = (4.0–10.6) \times 10^{-10}$ cm^3 s^{-1} molecule^{-1}. This, however, does not introduce unduly larger errors into the calculated K_1 value, since the four rate constants from the initial-rate method are utilized only to calculate a corrective term. The average value of K_1 from a large number of independent experiments is 25 ± 8, its uncertainty range being conservatively taken as the difference between the extreme values, rather than their (smaller) standard deviation. It is somewhat reassuring that the K_1 value deduced from the less accurate method based on the k_1:k_{-1} ratio measured in each experiment is 21 ± 6, which is not strikingly different from the 25 ± 8 value from the steady-state approach. From the latter value one derives $\Delta G_1° = -1.9 \pm 0.2$ kcal mol^{-1} at 298 K. Again, it is reassuring to note that the result is largely insensitive to errors affecting the measured K_1 value. As a matter of fact, doubling or halving K_1, which corresponds to errors far exceeding the estimated uncertainty range, would introduce an error of only ±0.4 kcal mol^{-1} into the derived $\Delta G_1°$ value.

As an aside, one notes that the rate constant of the NO_2^+ transfer (1) is approximately twice as large as the rate constant of the H^+ transfer (2), a feature discernible also in Figures 1 and 2, which justifies the choice of reaction (1) over more conventional prototropic equilibria.

Evaluation of $\Delta S_1°$, $\Delta H_1°$, and ΔPA. The $S°_{298}$ values of **1** and **2** have been estimated and combined with the known $S°_{298}$ values of H_2O and CH_3OH, 45.1 and 57.3 cal K^{-1} mol^{-1},[13] to calculate $\Delta S_1°$, required in turn to obtain $\Delta H_1°$. The more accurate approach has involved evaluation by standard procedures of the translational and rotational entropies of **1** and **2**, on the basis of their optimized geometries computed by Lee and Rice. The vibrational terms have likewise been calculated using theoretically computed harmonic frequencies.[9,10] Summation of the translation, rotational, and vibrational contributions gives $S°(\mathbf{1}) = 73.7$ and $S°(\mathbf{2}) = 83.2$ cal K^{-1} mol^{-1}, and hence $\Delta S_1° = -2.7$ cal K^{-1} mol^{-1} at 298 K. As concerns the accuracy of the result, it should be noted that the $S°_{298}$ values of the strictly related HNO_3 and CH_3ONO_2 molecules derived from the theoretically calculated[9,10] structures and harmonic frequencies are 63.6 and 71.1 cal K^{-1} mol^{-1}, in excellent agreement with the experimental values of 63.7 and 72.2 cal K^{-1} mol^{-1}, respectively.[13] Furthermore, the less accurate approach based on the replacement of **1** and **2** with suitable model molecules, *i.e.* HNO_3 and CH_3ONO_2, gives $\Delta S_1° = -2.3$ cal K^{-1} mol^{-1},[13] very close to the result from the above more accurate method. In summary, we estimate $\Delta S_1°$ to be -2.7 ± 1 cal K^{-1} mol^{-1} at 298 K, which combined with $\Delta G_1°$ gives $\Delta H_1° = -2.7 \pm 1$ kcal mol^{-1}. This quantity corresponds to the difference of the BEs of CH_3OH and of H_2O to NO_2^+ and can be used to evaluate ΔPA = PA(HNO_3) – PA(CH_3ONO_2). In fact, by combining **1** with the proton transfer reactions

$$H^+ + HNO_3 \rightarrow \mathbf{1} \tag{4}$$

$$H^+ + CH_3ONO_2 \rightarrow \mathbf{2} \tag{5}$$

and using the tabulated $\Delta H°_{f(298K)}$ values of CH_3OH, H_2O, HNO_3, and CH_3ONO_2,[5] one obtains $\Delta PA = \Delta H_1° + \Delta H_f°(CH_3OH) - \Delta H_f°(H_2O) + \Delta H_1°(HNO_3) - \Delta H_f°(CH_3ONO_2) = 4.0 \pm 2.3$ kcal mol^{-1}.

The PA of $C_2H_5ONO_2$. The discussion of the basicity trend in the $RONO_2$ series can benefit from the knowledge of the PA of $C_2H_5ONO_2$, whose only available value, 180 kcal mol^{-1}, was reported in 1970 as a result of early ICR bracketing experiments utilizing reference bases whose assigned PA has undergone in the meantime considerable changes.[14] As in the case of CH_3ONO_2, application of the equilibrium method is hindered by incursion of side reactions, in particular NO_2^+ transfer. As a consequence, reevaluation of the basicity of $C_2H_5ONO_2$ has been performed by FT-ICR spectrometry using the bracketing technique. The results indicate that the PA of $C_2H_5ONO_2$ is intermediate between those of C_3H_6 and C_2H_5OH, falling in the range from 178.4[15] to 188.3[5] kcal mol^{-1}. Furthermore, the study of the $C_2H_5ONO_2$/CH_3OH system has fortunately revealed, in addition to proton-transfer reactions occurring in both directions, the isotope exchange

$$CD_3OD + (C_2H_5ONO_2)H^+ \rightleftharpoons CD_3OH + (C_2H_5ONO_2)D^+ \tag{6}$$

The latter observation is particularly efficacious in showing that the PA of $C_2H_5ONO_2$ is close to that of CH_3OH, and hence it has confidently been assigned a value of 181.7 ± 2 kcal mol^{-1}.

Since no structural information is provided by the above experiments, and in the lack of theoretical studies on $(C_2H_5ONO_2)H^+$ ions, it is impossible at the present time to decide whether the measured PA of $C_2H_5ONO_2$ refers to formation of ions **3** or **6**.

Discussion

The results from the evaluation of equilibrium (1) are compared in Table 1 with those of previous experimental and theoretical studies. The *differences* between thermochemical quantities pertaining to the HNO_3 and to the CH_3ONO_2 systems are derived directly from the experimental measurements. These data, combined with the recently reevaluated[16] PA of CH_3ONO_2, have been utilized to calculate the PA of HNO_3 and the BEs of H_2O and CH_3OH to NO_2^+, reported in the first line of Table 1. It is apparent that the evaluation of the crucial difference between the PA of HNO_3 and of CH_3ONO_2 is affected by a substantially smaller uncertainty than previous experimental and theoretical estimates. A corresponding decrease of the experimental uncertainty in the evaluation of the *differences* of the BEs of H_2O and CH_3OH to NO_2^+ and of the heats of formation of **1** and **2** is also apparent from Table 1.

The absolute PA and BE values are appreciably less accurate than the ΔPA and ΔBE differences derived directly from the evaluation of equilibrium (1), owing to the combination of the errors affecting the PA of CH_3ONO_2 with those attached to the heats of formation of the relevant species, in particular NO_2^+ and CH_3ONO_2.[17]

---

(13) The $\Delta S°$ change of equilibrum 1 is approximated by the $\Delta S°$ change of the $HNO_3 + CH_3OH = CH_3ONO_2 + H_2O$ model reaction, which can be calculated from the $S°$ values of the species involved, taken from the following: Benson, S. W. *Thermochemical Kinetics*, 2nd ed; Wiley: New York, 1976. The $\Delta S_1°$ value obtained in this way, –3.7 cal K^{-1} mol^{-1}, is further corrected for the rotational entropy change that occurs in 1, but not in the model reaction, owing to the 2-fold symmetry axis present in $H_2O\text{-}NO_2^+$. The correction, *R* ln 2, leads to an estimated $\Delta S_1°$ of –2.3 cal K^{-1} mol^{-1}.

(14) Kriemler, P.; Buttrill, S. E., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 1123.

(15) The PAs of C_3H_6 and CH_3OH are those reported in a recent revision of the gas-phase PA scale by Szulejko and McMahon: Szulejko, I. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839.

(16) Ricci, A. *Org. Mass Spectrom.* **1994**, *29*, 55.

(17) The experimental errors (kcal mol^{-1}) attached to the relevant $\Delta H_f°$ values, are ±0.2 (NO_2^+), ±0.1 (CH_3OH and HNO_3), and ±1.1 (CH_3ONO_2). Cf. ref 11 and references therein.

Table 1. Thermochemical Data Relevant to Evaluation of the Relative PA of HNO_3 and CH_3ONO_2[a]

ΔPA[b]	Δ(BE)[c]	$\Delta(\Delta H_f°)$[d]	PA(HNO_3)	PA(CH_3ONO_2)	BE(NO_2^+–CH_3OH)	BE(NO_2^+–H_2O)	method	ref
4.0 ± 1.2	4.0 ± 2.3	6.9 ± 1.1	182.0 ± 2.3	178 ± 2[e]	22.3 ± 2.4	19.6 ± 2.4	FT-ICR	this work
2.7 ± 3.4	4.4 ± 3.3	5.6 ± 3.3	177.7 ± 2.3	175 ± 2.5	19.2 ± 2.3	14.8 ± 2.3	FA-CAD	11
5.6 ± 5	2.3 ± 4[f]		182.5 ± 3	176.9 ± 5	19.6 ± 2[f] (21.3)[g]	17.3 ± 2[f] (20.1)[g]	CCSD(T)+ZPVE	9, 10
			180			22	4-31G/6-31G**	2

[a] All data in kcal mol^{-1} and referred to 298 K, except where indicated. [b] ΔPA(HNO_3) – PA(CH_3ONO_2). [c] Δ(BE) = BE(NO_2^+–CH_3OH) – BE(NO_2^+–H_2O). [d] $\Delta(\Delta H_f°) = \Delta H_f°(2) - \Delta H_f°(1)$. [e] Experimental value from ref 16. [f] Referred to 0 K. [g] Value referred to 298 K, derived from the data of refs 9 and 10; see text.

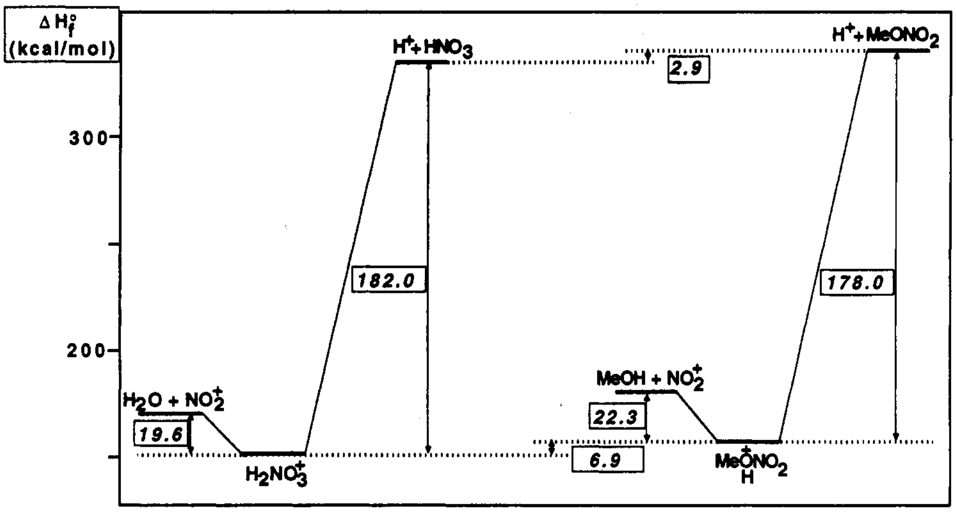


Figure 3. Schematic energy diagram of the H_2O-NO_2^+ and the CH_3OH-NO_2^+ systems.

The correspondence of the experimental results from the present study with those from the theoretical calculations of Lee and Rice[9,10] is striking. The BE and PA *differences* from this work agree within 0.4 and 1.3 kcal mol^{-1}, respectively, with their theoretical estimates, and the experimental PA of HNO_3 differs by only 0.5 kcal mol^{-1} from the value reported by Lee and Rice,[9] as shown in Table 1.

The only discrepancy that can be noted concerns the experimental BEs of H_2O and CH_3OH to NO_2^+ at 298 K, 19.6 and 22.3 kcal mol^{-1}, respectively, which are significantly larger than the corresponding values theoretically computed at 0 K, 17.3 and 19.6 kcal mol^{-1}. The discrepancy is only apparent because the two sets of values refer to different temperatures. In the lack of theoretically computed BE_{298} data, approximate values, much closer to those from this study and reported in parentheses in Table 1, can be estimated from the PAs of HNO_3 and CH_3ONO_2 at 298 K, reported in the theoretical study of Lee and Rice.[18] Whereas the accuracy of such indirectly evaluated BEs is questionable, the very nature of the reactions leading to dissociation of **1** and **2** suggests that their endothermicity, which corresponds to the BE, should *increase* in passing from 0 to 298 K. In summary, the agreement of the experimental results is excellent, and bears witness to the powers of high-level *ab initio* methods.

Turning to the question addressed in the title, the results illustrated in Figure 3 support the theoretically predicted trend of the PA of HNO_3 and CH_3ONO_2.[10] The experimental verification rests now on firm grounds, since the direct link between the basicity of the two molecules established by equilibrium (1) has allowed the relatively small PA difference to be evaluated with adequate accuracy.

The trend of the PA of $RONO_2$ molecules, which decreases from HNO_3 to CH_3ONO_2, increasing again in passing to $C_2H_5ONO_2$, is not easily understood. The explanation offered by Lee and Rice, who correlate the PA of $RONO_2$ molecules with the difference between the RO–H and the RO–NO_2 bond energies,[10] holds for the HNO_3/CH_3ONO_2 pair but apparently fails to account for the PA increase of 3.7 kcal mol^{-1} noted in passing from CH_3ONO_2 to $C_2H_5ONO_2$. A possible complication is the reversal of the stability order of the protomers, in that **6** could conceivably be more stable than complex **3**, at variance with the situation prevailing with R = H or CH_3. This view is consistent with the decrease of the stability difference between ROH-NO_2^+ and $RONO_2H^+$ isomers, calculated by Lee and Rice to drop from 20 (R = H) to 4.9 (R = CH_3) kcal mol^{-1}.[10] Elucidation of this problem seems well within the reach of current experimental and high-level *ab initio* techniques and may prove of considerable value to a better understanding of the relative PA of $RONO_2$ molecules.

A final point deserves a brief discussion, aimed at explaining the results of our earlier bracketing experiments conducive to PA(HNO_3) = 168 ± 3 kcal mol^{-1}.[4] The assignment of the upper limit of the PA bracket was based on the observation that the population of $(HNO_3)H^+$ ions from low-exothermicity reactions known to give ions of structure **1** protonates CF_3CH_2OH, PA = 169 kcal mol^{-1}.[5] A plausible explanation can be based on the fact, now firmly established, that complex **1**, while *thermochemically* more stable, undergoes facile dissociation into H_2O and NO_2^+, whereas the isomer **4** is *kinetically* stable, owing to its higher barrier to rearrangement and/or loss of H_2O.[4] This specific situation is particularly unfavorable to the correct application of the bracketing technique. In fact, in the early ICR experiments, even a minor initial contamination of the $(HNO_3)H^+$ population by ions of structure **4** could become troublesome in that their relative abundance steadily increased owing to extensive decomposition of ions **1** during the time required by their collisional-cooling and isolation steps *before* proton transfer occurred. Despite the vastly improved techniques currently available and applied in this work in order to thermalize ions **1**, their decomposition into NO_2^+ and H_2O is still detectable,

---

(18) The theoretically calculated PAs of HNO_3 and CH_3ONO_2 at 298 K from ref 10, combined with the heats of formation at 298 K of H^+, HNO_3, and CH_3ONO_2, allow one to evaluate $\Delta H_f°$ of **1** and **2** at 298 K. The latter values are combined with the heats of formation at 298 K of NO_2^+, H_2O, and CH_3OH to obtain the BEs of H_2O and CH_3OH to NO_2^+ at 298 K.

e.g. in Figures 1 and 2. In this light, it is suggested that in the early ICR experiments ions of structure **4** were responsible for the observed proton transfer from $(HNO_3)H^+$ to CF_3CH_2OH and hence that the value of 168 ± 3 kcal mol^{-1}, then taken as the PA of HNO_3 and referred to formation of protomer **1**, represents instead an upper limit of the PA of the nitro group of HNO_3, *being referred to formation of the less stable protomer 4.*

Experimental Section

The chemicals used were research-grade samples from Matheson Gas Products Inc. and Aldrich Chemical Co. Inc. or were prepared and purified according to standard procedures. The gaseous H_2O/CH_3OH mixtures required for the study of equilibrium (1) were obtained as follows: dilute aqueous solutions of methanol were prepared by mixing carefully measured amounts of the components, then introduced into Pyrex vessels, frozen at −196 °C, and outgassed in a vacuum line by repeated freeze–thaw cycles. The solutions were then allowed to equilibrate with their vapor at 25 °C, and a small fraction of the gas phase above the liquid was leaked into the cell of the ICR spectrometer. The (corrected) readings of the ionization gauge were taken as a measurement of $p(H_2O)$. In so doing, one neglects the contribution to the total pressure, the quantity actually measured by the gauge, of $p(CH_3OH)$. Given the high $p(H_2O)$:$p(CH_3OH)$ ratios, ranging from 30 to 50, the error introduced in this way is small and does not affect the evaluation of K_1. From $p(H_2O)$ one can evaluate $p(CH_3OH)$, since the $p(CH_3OH)$:$p(H_2O)$ ratio in the vapor phase in equilibrium with a liquid CH_3OH/H_2O mixture of defined composition and temperature is known with adequate accuracy.[19] The mass spectrometric measurements were performed using an APEX TM 47e instrument from Bruker Spectrospin, equipped with an "infinity cell", a 4.7-T superconducting magnet, an external EI/CI ion source, two pulsed valves, and a XMASS TM data system.

Acknowledgment. We thank F. Grandinetti and A. Ricci for their invaluable help and many useful discussions, and Prof. R. R. Squires for a preprint of his paper. The financial support of Italian Ministero per l'Università e la Ricerca Scientifica e Tecnologica (MURST) and Consiglio Nazionale delle Ricerche (CNR) is gratefully acknowledged.

---

(19) Given the low concentrations of CH_3OH, the composition of the vapor in equilibrium with each solution obeys with sufficient accuracy the Raoult law. This has been checked by comparing the calculated vapor composition with those reported in standard compilations. Cf.: Timmermans, J. *The Physico-Chemical Constants of Binary Systems in Concentrated Solutions*; Interscience Publ., Inc.: New York, 1960, Vol. 4, p 153.