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A comprehensive computational investigation of the enthalpies of formation and proton affinities of C_4H_7N and C_3H_3ON compounds

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Abstract

The results of electronic structure studies aimed at determining accurate enthalpies of formation and proton affinities for a comprehensive set of C_4H_7N and C_3H_3ON compounds are reported. The calculated thermodynamic values are rationalized in terms of the nitrogen functionality and the influence of unsaturated C–C bonding environments. Using these results, it is proposed that a previously unidentified mass 70 amu tropospheric ion is the protonated form of 1-pyrroline, an unsaturated nitrogen heterocyclic compound emitted into the atmosphere by both plant and animal biological activity.

Keywords: Tropospheric chemistry; Enthalpy of formation; Proton affinity

1. Introduction

During the past two decades, there has been considerable progress made in the identification of ions in the troposphere. The first ground level tropospheric measurements were reported by Eisele in 1983 [1], who discovered the presence of positive ions with mass 80 and 94 amu. In the intervening period, many more tropospheric positive ions have been discovered [2–8], and some of these have been definitively identified [9]. While the role of ions in atmospheric chemistry may include reactions that directly influence tropospheric composition through ion–molecule reactions, it has been recently suggested that such ions may play a key role in the nucleation mechanisms that lead to the formation of aerosol particles [10], which are known to play key roles in heterogeneous atmospheric chemistry and in the regulation of the earth's climate. In an attempt to better understand these processes, Beig and Brasseur recently proposed a model of tropospheric ion composition [11]. While the model was successful in some respects, Beig and Brasseur noted that it will be necessary to make more accurate measurements and to identify more of the unidentified ions in order to fully evaluate the accuracy of the model.

The identification of tropospheric ions has largely relied on tandem mass spectrometric measurements, and the mechanisms of ion formation that have been postulated to explain these observations are based on a combination of kinetic and thermodynamic arguments. The tandem mass spectrometry method for the identification of tropospheric ions uses the following protocol: (1) the sampled cluster ions are stripped of

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their neutral ligands in a collisional dissociation chamber; (2) a particular parent ion is selected by passing it through a quadrupole mass filter; (3) this parent ion is accelerated into a buffer gas to cause fragmentation; (4) the fragments are then mass analyzed with another quadrupole mass filter resulting in what is known as the daughter ion spectrum. The identity of a tropospheric ion is then confirmed by matching its daughter ion spectrum to that of the daughter ion spectrum of an artificially prepared (and known) ion. As an example, this technique has been used to establish that the mass 80 and 94 amu positive ions originally measured by Eisele and Tanner are the protonated ions of pyridine and methyl pyridine (picoline) [9].

It is now postulated that the mechanism that best explains observed tropospheric positive ion composition begins with a cosmic ray- or radioactive decay-initiated production of $H^+(H_2O)_n$ ions. These ions subsequently react (usually by ligand-switching reactions) with successively less abundant trace neutral species to form progressively more stable atmospheric ions. For example, Beig and Brasseur assume in their model that protonated pyridine is mainly produced via these type of these reactions of pyridine with protonated ammonia complexes [11]. The protonated ammonia complexes are formed via ligand-switching reactions with the precursor $H^+(H_2O)_n$ ions mentioned above. For example, the following ligand-switching reaction

$$H^+(H_2O)_n + NH_3 \rightarrow H^+(NH_3)(H_2O)_{n-2} + 2H_2O \quad (1)$$

(and similar reactions that lead to more substitution of ammonia for water) can lead to the production of protonated ammonia clusters. Viggiano et al. have shown that these species react very efficiently (at the collision-limited rate) with pyridine [12]:

$$\begin{aligned} &H^+(NH_3)_m(H_2O)_n + \text{pyridine} \\ &\quad \rightarrow H^+(\text{pyridine})(NH_3)_{m-y}(H_2O)_{n-x} \\ &\qquad + yNH_3 + xH_2O \end{aligned} \quad (2)$$

The driving force in the ligand-switching reactions is the larger proton affinity (PA) of inserting ligand as compared to the leaving ligand. Thus, in reactions (1) and (2), H_2O (PA: 691 kJ/mol) is replaced by NH_3 (PA: 854 kJ/mol), which is replaced by pyridine (PA: 930 kJ/mol) in the ion [13]. The direct reaction

$$\begin{aligned} &H^+(H_2O)_n + \text{pyridine} \\ &\quad \rightarrow H^+(\text{pyridine})(H_2O)_{n-x} + xH_2O \end{aligned} \quad (3)$$

is also known to be fast [14], but because ammonia is much more abundant than pyridine in the atmosphere, it is expected that primary fate of $H^+(H_2O)_n$ ions is reaction with ammonia (such as in reaction (1)). In fact, it has been observed that all other identified tropospheric ions have neutral parent species with higher proton affinities than NH_3, thus suggesting that reaction (2) must be the dominant type of ion formation mechanism for all tropospheric ions containing neutral precursors other than H_2O and NH_3 discovered so far. Therefore, the atmospheric abundance of tropospheric ions determined by both kinetic and thermodynamic effects. For the abundant neutral precursors (H_2O and NH_3), kinetic effects lead to relatively large tropospheric abundances of ions containing these species. However, thermodynamic driving forces tend to lead to tropospheric ions which have neutral precursors with larger proton affinities than H_2O or NH_3. Thus, the thermodynamic driving force to form the most stable positive ions can lead to the observation of ions which contain parent neutral species of relatively low atmospheric abundance (such as pyridine). This aspect makes the identification of tropospheric ions challenging because trace neutral compounds can be the precursors for relatively abundant tropospheric ions. However, if the thermodynamic driving forces can be predicted for a particular ion formation mechanism (i.e., proton affinity values are the most important information), the process of identifying tropospheric ions can be made more manageable.

As mentioned above, there are still a number of tropospheric ions that have yet to be identified. The measurements of Eisele have repeatedly revealed the presence of a positive ion with mass 70 amu [5]. It is important to recall the tandem mass spectrometry method employed by Eisele strips away all neutral ligands, so that only the core ion remains. This simplifies the analysis, as the parent neutral species of the mass 70 amu ion therefore unambiguously has a mass of 69 amu. It is clear that this species contains nitrogen, as the parent neutral species has an odd mass, and the daughter ion spectrum has a large peak at mass 29 amu, which is often associated with the CH_2N^+ fragment ion. Through tandem mass spectrometry measurements of just a few of the many possible compounds with a protonated mass of 70 amu, Eisele tentatively identified this tropospheric ion as protonated isoxazole ($C_3H_3ONH^+$). However, it was noted that daughter ion spectrum of protonated isoxazole was not a very good match with the daughter ion spectrum of the mass 70 amu ion. In addition, Eisele pointed out that the isoxazole proton affinity is lower than that of NH_3. If isoxazole were in fact the neutral parent compound of the mass 70 amu ion, it would be the first example of an identified tropospheric ion with a parent proton affinity less than that of NH_3. Therefore, for these reasons, Eisele considered the identification of the mass 70 amu ion as protonated isoxazole to be tentative.

In recent years, the method of proton transfer reaction mass spectrometry (PTR-MS) has been adopted for use in a wide range of chemical applications, particularly those which involve the measurement of volatile organic compounds (VOCs). A recent review on the technique included examples of the use of the method in such areas as breath analysis, food research, and atmospheric chemistry [15]. In this technique, neutral compounds are detected via mass spectrometry as the proton transfer products of a reaction with a molecular ion, usually H_3O^+. This approach is powerful because of the wide range of compounds that react with H_3O^+, and the fact that this (chemical ionization) reaction is often non-dissociative, which makes the interpretation of the resulting mass spectrum more straightforward. The selectivity of the technique is almost completely determined by the proton affinity of the neutral compounds relative to that of water (i.e., the proton transfer reactions are thermodynamically driven when the analyte proton affinity is larger than that of water). Indeed, if the analyte proton affinity is too high compared to that of water, dissociation of the molecular ion can occur. Therefore, there is a need for accurate proton affinities of all classes of compounds that may be potentially detected in PTR-MS applications.

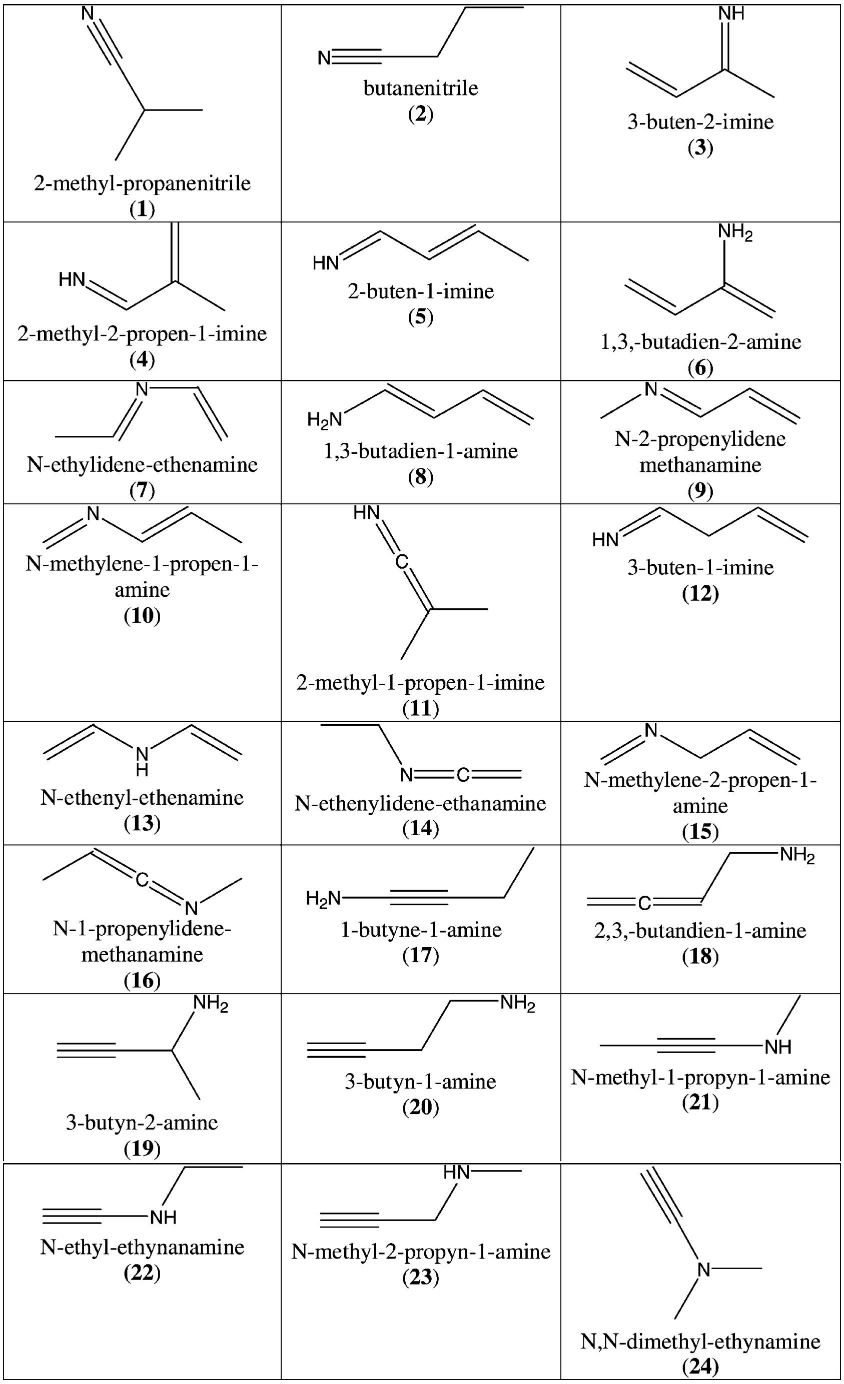
It is the purpose of this work to use computational thermodynamic methods to investigate the potential identity of the mass 70 amu ion. As will be discussed below, the neutral parent is likely to have a molecular formula of C_4H_7N or C_3H_3ON. The enthalpies of formation and proton affinities of 78 compounds possessing either of these molecular formulas are calculated in an effort to narrow down the number of species that might be responsible for the mass 70 amu ion observed in tropospheric field measurements. As an added benefit, this systematic exploration of thermodynamic parameters for several different classes of nitrogen-containing molecules should provide fundamental information on the stability and reactivity of these relatively unstudied species. In addition, the proton affinity values should be useful to PTR-MS practitioners who may encounter these compounds in their own research setting.

2. Computational methods

2.1. Modified G2MS method

To facilitate accurate calculations of the enthalpies of formation and proton affinities for a large number of compounds, the energies of the relevant species were calculated using an adapted version of the G2MS compound method [16], a variation on G2 theory [17]. The geometries were optimized and vibrational frequencies were obtained from analytical derivatives calculated at the B3LYP/6-31G(d,p) level of theory and each stationary point was confirmed as a potential energy minimum by inspection of the calculated frequencies. The overall energy expression for our implementation of the G2MS scheme is defined as

$$\begin{aligned} E(\mathrm{G2MS}) = {} & E[\mathrm{CCSD(T)/6\text{-}31G(d)}] \\ & + E[\mathrm{MP2/6\text{-}311+G(2df,2p)}] \\ & - E[\mathrm{MP2/6\text{-}31G(d)}] + \mathrm{HLC} \end{aligned} \qquad (4)$$



2-methyl-propanenitrile **(1)**
butanenitrile **(2)**
3-buten-2-imine **(3)**
2-methyl-2-propen-1-imine **(4)**
2-buten-1-imine **(5)**
1,3,-butadien-2-amine **(6)**
N-ethylidene-ethenamine **(7)**
1,3-butadien-1-amine **(8)**
N-2-propenylidene methanamine **(9)**
N-methylene-1-propen-1-amine **(10)**
2-methyl-1-propen-1-imine **(11)**
3-buten-1-imine **(12)**
N-ethenyl-ethenamine **(13)**
N-ethenylidene-ethanamine **(14)**
N-methylene-2-propen-1-amine **(15)**
N-1-propenylidene-methanamine **(16)**
1-butyne-1-amine **(17)**
2,3,-butandien-1-amine **(18)**
3-butyn-2-amine **(19)**
3-butyn-1-amine **(20)**
N-methyl-1-propyn-1-amine **(21)**
N-ethyl-ethynanamine **(22)**
N-methyl-2-propyn-1-amine **(23)**
N,N-dimethyl-ethynamine **(24)**

Fig. 1. Structures, names, and labels for aliphatic C_4H_7N compounds under study.

where HLC is an empirically defined correction term with $\mathrm{HLC} = An_\alpha + Bn_\beta$ where n_α and n_β are the number of α and β electrons, respectively. The constants A and B are defined as 6.06 and 0.19 mH, respectively. In order to calculate standard (1 atm, 298 K) enthalpies, vibrational frequencies recovered from B3LYP/6-31G(d,p) calculations were used in conjunction with statistical thermodynamic methods.

The standard enthalpies of formation for the species under study (X) were calculated from the atomization energies as follows [18]:

$$\Delta H_\mathrm{f}^\circ(X) = H(X) + \sum_I n_I(X)[\Delta H_\mathrm{f}^\circ(I) - H(I)] \quad (5)$$

where $n_I(X)$ is the number of atoms of the element I present in X and $\Delta H_\mathrm{f}^\circ(I)$ is the standard enthalpy of formation of I. The enthalpies $H(X)$ and $H(I)$ of X and I and standard temperature are sums of three terms:

$$H(A) = E(A) + E_\mathrm{ZP}(A) + E_\mathrm{therm}(A), \quad A = X \text{ or } I \quad (6)$$

where E and E_ZP are the total and zero-point energies, respectively, and E_therm is the difference between the enthalpy at standard temperature and the energy at absolute zero temperature. $H(X)$ and $E(I)$ were calculated via the G2MS method described above, and the experimental $\Delta H_\mathrm{f}^\circ(I)$ and $E_\mathrm{therm}(I)$ (to allow calculation of $H(I)$ from Eq. (6)) values for the atoms were used [19].

The proton affinities were calculated from the standard enthalpies of the neutral and cation species. We have previously shown that this method provides excellent accuracy (<10 kJ/mol error) in the calculation of thermodynamic quantities for compounds similar to those under study here [20].

2.2. Selection of compounds for study

The only neutral compounds that appear in the ACS registry (searched via the Chemical Abstracts SciFinder Scholar interface) with mass 69 amu and an odd number of nitrogen atoms have the molecular formula C_4H_7N or C_3H_3ON. Therefore, the search for the identity of the mass 70 amu tropospheric ion was limited to neutral parent compounds with one of these two molecular formulas. All compounds from the ACS registry with molecular formula C_4H_7N and C_3H_3ON were included in the present study with the exception of radicals, ions and non-naturally abundant isotopomers (these types of species are not abundant enough in the atmosphere to be possible neutral parents of the mass 70 amu ion). In all, 47 C_4H_7N and 31 C_3H_3ON compounds were investigated, for a total of 78 species. To aid in the presentation of results, the C_4H_7N compounds were separated into two groups: aliphatic and cyclic structures. The chemical structures and names of the species studied are presented in Figs. 1–3.

3. Results and discussion

The optimized geometries, energies and vibrational frequencies for all species are available via the Internet [21].

3.1. Enthalpies of formation

For the C_4H_7N compounds, the accuracy of the atomization approach can be evaluated by comparing the standard enthalpies of formation calculated via this method for the three C_4H_7N compounds for which there are experimental values, 2-methyl-propanenitrile (22 kJ/mol) [22], butanenitrile (31 kJ/mol) [23], and 1-pyrroline (63 kJ/mol) [24]. The calculated standard enthalpies of formation for these compounds are 30, 35, and 73 kJ/mol, respectively, which are all within 10 kJ/mol of the experimental values. The calculated standard enthalpies of formation for the aliphatic C_4H_7N compounds are given in Table 1 and the similar values for the cyclic C_4H_7N compounds are given in Table 2. For the C_3H_3ON compounds, experimental standard enthalpies of formation values are available only for oxazole (−16 kJ/mol) and isoxazole (79 kJ/mol) [25]. The computational results for these compounds were found to be −14 and 82 kJ/mol, respectively, in excellent agreement with experimental values. The calculated standard enthalpies of

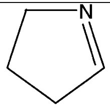
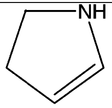
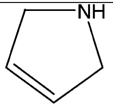
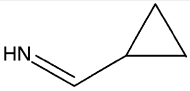
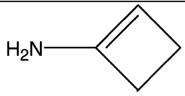
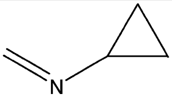
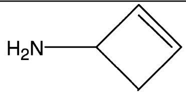
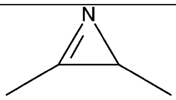
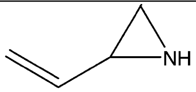
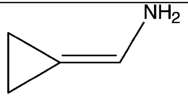
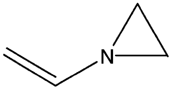
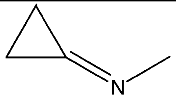
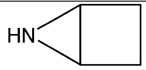
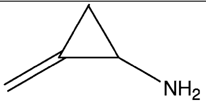
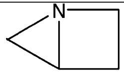
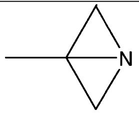
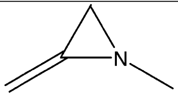
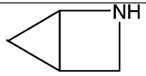
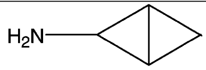
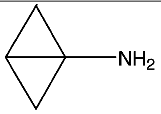
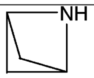
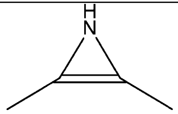
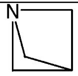
 1-pyrroline (**1**)	 2-pyrroline (**2**)	 3-pyrroline (**3**)
 cyclopropanemethanimine (**4**)	 1-cyclobuten-1-amine (**5**)	 cyclopropane methanimine (**6**)
 2-cyclobuten-1-amine (**7**)	 2,3-dimethyl-2H-azirine (**8**)	 2-ethenyl-aziridine (**9**)
 cyclopropylidene-methylamine (**10**)	 1-ethenyl-aziridine (**11**)	 N-cyclopropylidine methanamine (**12**)
 5-azabicyclo[2.1.0]pentane (**13**)	 2-methylene-cyclopropanamine (**14**)	 1-azabicyclo[2.1.0]pentane (**15**)
 3-methyl-1-azabicyclo[1.1.0]butane (**16**)	 1-methyl-2-methylene-aziridine (**17**)	 2-azabicyclo[2.1.0]pentane (**18**)
 bicyclo[1.1.0]butan-2-amine (**19**)	 bicyclo[1.1.0]butan-1-amine (**20**)	 2-azabicyclo[1.1.1]pentane (**21**)
 2,3-dimethyl-1H-azirine (**22**)	 1-azabicyclo[1.1.1]pentane (**23**)	

Fig. 2. Structures, names, and labels for cyclic C_4H_7N compounds under study.

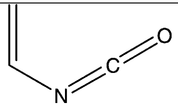
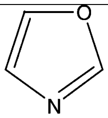
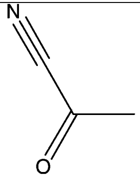
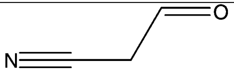
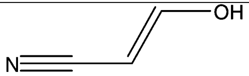
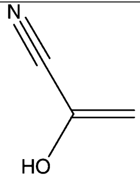
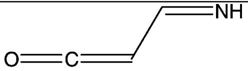
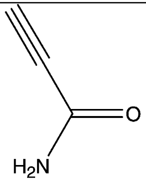
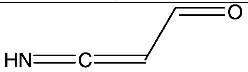
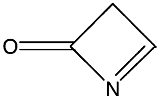
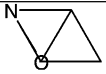
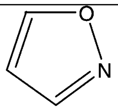
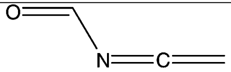
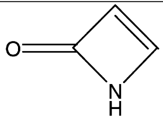
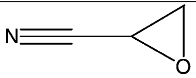
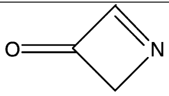
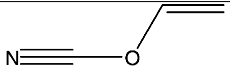
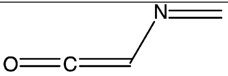
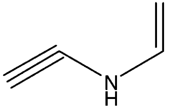
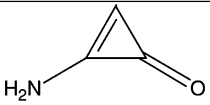
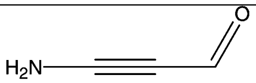
 isocyanato-ethene (**1**)	 oxazole (**2**)	 2-oxo-propanenitrile (**3**)
 3-oxo-propanenitrile (**4**)	 3-hydroxy-2-propenenitrile (**5**)	 2-hydroxy-2-propenenitrile (**6**)
 3-imino-1-propen-1-one (**7**)	 2-propynamide (**8**)	 3-imino-2-propenal (**9**)
 2(3H)-azetone (**10**)	 3-oxa-2-azatricyclo[2.1.0.02,5] pentane (**11**)	 isoxazole (**12**)
 N-ethenylidene-formamide (**13**)	 2(1H)-azetone (**14**)	 oxiranecarbonitrile (**15**)
 3(2H)-azetone (**16**)	 cyanic acid ethenyl ester (**17**)	 (methyleneamino)-ethenone (**18**)
 N-ethynyl-formamide (**19**)	 2-amino-2-cyclopropen-1-one (**20**)	 3-amino-2-propynal (**21**)

Fig. 3. Structures, names, and labels for C_3H_3ON compounds under study.

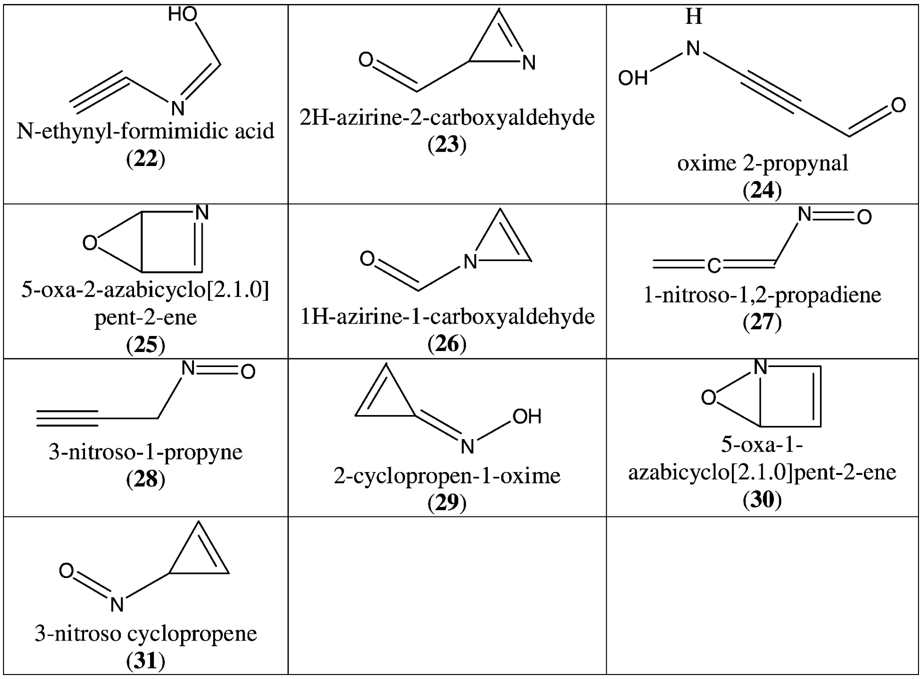


Fig. 3. (*Continued*).

formation for the C_3H_3ON compounds are given in Table 3.

Due to the systematic study of a relatively large number of compounds, some general trends in the thermodynamic stability (enthalpy of formation) are evident in Tables 1–3. It is useful to note that the C_4H_7N compounds have an unsaturation number of 2 and the C_3H_3ON compounds have an unsaturation number of 3, which is manifested in the occurrence of cyclic structures and double and triple bonds. In general, the most stable C_3H_3ON compounds were more stable than the most stable aliphatic C_4H_7N compounds, which were more stable than the most stable cyclic C_4H_7N compounds. Within the aliphatic C_4H_7N series, the following general functional group dependence is observed (in order of increasing enthalpy of formation): (1) nitriles, (2) imines and amines derived from butadiene, (3) primary amines derived from butyne. For the cyclic C_4H_7N species, the pyrrolines (singly unsaturated five-membered nitrogen heterocycles) were found to be significantly more stable than the other species. For the C_3H_3ON species, with the exception of oxazole (a doubly unsaturated five-membered oxygen and nitrogen heterocycle) and isocyanato-ethene, the most stable species tended to possess nitrile functionality. The imines were also found to be relatively stable and the nitroso compounds were found to be the least stable. Therefore, it is clear that within the group of compounds considered, thermodynamic stability is conferred upon species which (wholly or partially) satisfy their unsaturation number requirements by using nitrogen atoms in double and triple bonding situations ($R{=}NH$, $R{-}N{=}R'$, or $R{\equiv}N$). This observation can be understood from a consideration of the relative mean bond enthalpies for C–C and C–N bonds. The C–C single bond enthalpy is greater than that for C–N single bonds (348 vs. 305 kJ/mol), the C–C and C–N double bond enthalpies are approximately equal (612 vs. 613 kJ/mol), and the C–C triple bond enthalpy is less than that for C–N triple bonds (838 vs. 890 kJ/mol) [26]. Therefore, greater thermodynamic stability is

Table 1
Standard enthalpies of formation and proton affinities for aliphatic C_4H_7N compounds

Compound	Name	ΔH_f (kJ/mol)	PA (kJ/mol)
1	2-Methyl-propanenitrile	30.3	796.2
2	Butanenitrile	35.4	793.1
3	3-Buten-2-imine	100.6	934.6
4	2-Methyl-2-propen-1-imine	101.1	918.0
5	2-Buten-1-imine	105.2	933.5
6	1,3-Butadien-2-amine	113.5	869.0
7	*N*-Ethylidene-ethenamine	121.8	911.9
8	1,3-Butadien-1-amine	129.1	865.4
9	*N*-2-Propenylidene methanamine	131.4	929.8
10	*N*-Methylene-1-propen-1-amine	135.7	896.4
11	2-Methyl-1-propen-1-imine	139.4	875.3
12	3-Buten-1-imine	142.2	927.5
13	*N*-Ethenyl-ethenamine	144.0	857.1
14	*N*-Ethenylidene-ethanamine	160.3	868.7
15	*N*-Methylene-2-propen-1-amine	162.0	901.5
16	*N*-1-Propenylidene-methanamine	168.8	884.8
17	1-Butyn-1-amine	196.8	825.1
18	2,3-Butadien-1-amine	198.3	907.3
19	3-Butyn-2-amine	202.9	900.5
20	3-Butyn-1-amine	203.4	888.3
21	*N*-Methyl-1-propyn-1-amine	224.3	799.4
22	*N*-Ethyl-ethynamine	228.9	844.4
23	*N*-Methyl-2-propyn-1-amine	234.1	916.0
24	*N*,*N*-Dimethyl-ethynamine	254.7	796.4

achieved by increasing the bond order for bonds involving nitrogen, as opposed to bonds involving only carbon.

3.2. Proton affinities

The calculated proton affinities for the aliphatic, ring C_4H_7N, and C_3H_3ON species are presented in Tables 1–3, respectively. Although numerous studies of carbon, oxygen and nitrogen-containing compounds have repeatedly indicated the strong preference for protonation at the nitrogen atom, protonation at all ring positions was explicitly considered for the case of the C_3H_3ON heterocyclic species, isoxazole. Protonation at the three unique carbon atoms and the oxygen atom was found to lead to proton affinities more than 100 kJ/mol lower than the proton affinity calculated at the nitrogen atom position. Therefore, only cation species with protonation at the nitrogen atom were considered in the calculation of proton affinities. There are experimental values available for comparison for only 4 of the 78 compounds considered: 2-methyl-propanenitrile (804 kJ/mol) butanenitrile (798 kJ/mol), oxazole (876 kJ/mol), and isoxazole (847 kJ/mol) [13]. As expected, the MG2MS method performs well, with all four of these proton affinities calculated to within 10 kJ/mol of the experimental values.

Trends were also apparent in the calculated proton affinities given in Tables 1–3. As a group, the cyclic C_4H_7N compounds had higher proton affinities than the aliphatic C_4H_7N or C_3H_3ON compounds. Within the aliphatic C_4H_7N compounds, the imines derived from butadiene tended to have the highest proton affinities, while the nitriles had the lowest values. The amine proton affinities depended directly on the proximity of double or triple bond C–C functionality. For example, amines bonded to carbons involved in C–C triple bonds were found to have the lowest proton affinities. For the larger cyclic (four or five

Table 2
Standard enthalpies of formation and proton affinities for cyclic C_4H_7N compounds

Compound	Name	ΔH_f (kJ/mol)	PA (kJ/mol)
1	1-Pyrroline	72.7	925.8
2	2-Pyrroline	101.1	909.0
3	3-Pyrroline	118.7	931.0
4	Cyclopropanemethanimine	150.5	918.5
5	1-Cyclobuten-1-amine	158.0	866.2
6	*N*-Methylene-cyclopropanamine	180.1	898.8
7	2-Cyclobuten-1-amine	186.3	907.6
8	2,3-Dimethyl-2*H*-azirine	186.7	859.7
9	2-Ethenyl-aziridine	199.0	906.1
10	Cyclopropylidene-methylamine	207.1	887.1
11	1-Ethenyl-aziridine	215.4	903.6
12	*N*-Cyclopropylidene methanamine	222.4	931.1
13	5-Azabicyclo[2.1.0]pentane	225.6	915.5
14	2-Methylene-cyclopropanamine	225.6	898.3
15	1-Azabicyclo[2.1.0]pentane	238.9	930.9
16	3-Methyl-1-azabicyclo[1.1.0]butane	239.3	893.4
17	1-methyl-2-methylene-aziridine	248.1	908.3
18	2-Azabicyclo[2.1.0]pentane	250.8	941.0
19	Bicyclo[1.1.0]butan-2-amine	253.1	893.3
20	Bicyclo[1.1.0]butan-1-amine	254.9	878.2
21	2-Azabicyclo[1.1.1]pentane	289.5	947.5
22	2,3-Dimethyl-1*H*-azirine	310.9	976.6
23	1-Azabicyclo[1.1.1]pentane	316.7	943.5

atom rings) C_4H_7N amines (including the pyrroline family), the largest proton affinities were calculated for the amines directly involved in cyclic bonding situations. The primary amines tended to have the lowest proton affinity values. The C_3H_3ON proton affinity trends were similar to those for the aliphatic C_4H_7N compounds in that imines were found to possess high proton affinities and nitriles tended to have the lowest proton affinity values. To summarize, imines were generally found to have the largest proton affinities and nitriles were found to have the lowest proton affinities, and the amines were found to have proton affinities that depended significantly on the hybridization of the proximate carbon atoms.

In general, for nitrogen-containing compounds with saturated aliphatic functionality, the amines are known to have the highest proton affinities and nitriles are known to have the lowest proton affinities, with imines having intermediate proton affinity values [13]. These trends have been investigated through a number of theoretical studies. In particular, Ijjaali et al. [27] performed a systematic study of the effect of differing hybridization of the basic center on the proton affinities for nitrogen and phosphorus compounds. The calculated proton affinities were found to correlate with the hybridization of the basic center as is observed experimentally: proton affinity (amines) $>$ proton affinity (imines) $>$ proton affinity (nitriles). Indeed, Ijjaali et al. found a strong linear relationship between the intrinsic basicities and charge densities at the basic center, confirming the conceptual notion that basicity correlates with increased ‘p’ character in the lone pairs.

Experimental [28,29] and theoretical investigations [30,31] of the proton affinities of imines have also been carried out which serve to explain some of the same trends described for the compounds under study in this work. In particular, because the basicity of the imines is enhanced by resonance stabilization, it has shown that the electronic character of neighboring groups has a very significant effect on the basicity of the basic center in imines. Thus, the presence of

Table 3
Standard enthalpies of formation and proton affinities for C_3H_3ON compounds

Compound	Name	ΔH_f (kJ/mol)	PA (kJ/mol)
1	Isocyanato-ethene	−17.6	743.2
2	Oxazole	−14.3	867.8
3	2-Oxo-propanenitrile	−14.2	732.9
4	3-Oxo-propanenitrile	−6.7	767.1
5	3-Hydroxy-2-propenenitrile	8.3	814.4
6	2-Hydroxy-2-propenenitrile	19.8	764.7
7	3-Imino-1-propen-1-one	45.9	914.1
8	2-Propynamide	61.9	774.2
9	3-Imino-2-propenal	63.7	772.0
10	2(3*H*)-azetone	65.5	846.4
11	3-Oxa-2-azatricyclo[2.1.0.02.5]pentane	82.2	836.5
12	Isoxazole	82.3	836.6
13	*N*-Ethenylidene-formamide	82.6	803.4
14	2(1*H*)-Azetone	89.4	957.6
15	Oxiranecarbonitrile	95.9	752.9
16	3(2*H*)-Azetone	98.1	825.8
17	Cyanic acid ethenyl ester	101.7	782.6
18	(Methleneamino)-ethenone	108.5	862.0
19	*N*-Ethynyl-formamide	111.4	720.3
20	2-Amino-2-cyclopropen-1-one	129.0	747.8
21	3-Amino-2-propynal	134.0	748.5
22	*N*-Ethynyl-formimidic acid	152.3	850.6
23	2*H*-Azirine-2-carboxaldehyde	159.0	770.3
24	Oxime-2-propynal	262.4	812.7
25	5-Oxa-2-azabicyclo[2.1.0]pent-2-ene	272.0	856.4
26	1*H*-Azirine-1-carboxaldehyde	281.1	879.4
27	1-Nitroso-1,2-propadiene	320.5	806.9
28	3-Nitroso-1-propyne	328.6	754.2
29	2-Cyclopropen-1-oxime	357.4	905.3
30	5-Oxa-1-azabicyclo[2.1.0]pent-2-ene	371.5	804.9
31	3-Nitroso-cyclopropene	388.2	811.3

unsaturated C–C bonds near the basic center in imines would be expected to influence proton affinities, as they could affect the resonance stabilization of the protonated species. This is the likely explanation for our finding that the imines studied in this work generally had higher proton affinities than the amines that were investigated.

3.3. Identity of mass 70 amu tropospheric ion

The work of Eisele and Tanner [9] strongly indicates that the mass 70 amu tropospheric ion must possess a proton affinity that is greater than that of NH_3 (854 kJ/mol) [13], as no other identified tropospheric ions are derived from neutral compounds with proton affinities lower than NH_3. In addition, it might also be expected that more stable neutral species are more likely to formed and persist in the atmosphere and build up to concentrations such that their reactions with precursor ions become kinetically feasible. Thus, it might be expected that neutral species with lower enthalpies of formation are more likely candidates as parents to the mass 70 amu tropospheric ion. However, as discussed in the introduction, the kinetics of the ion formation might be fast enough such that the thermodynamically most favorable ionic species are formed even from neutral species of low concentration. Therefore, a strong constraint on the identity of the mass 70 amu tropospheric ion is a proton affinity for the parent neutral species in excess

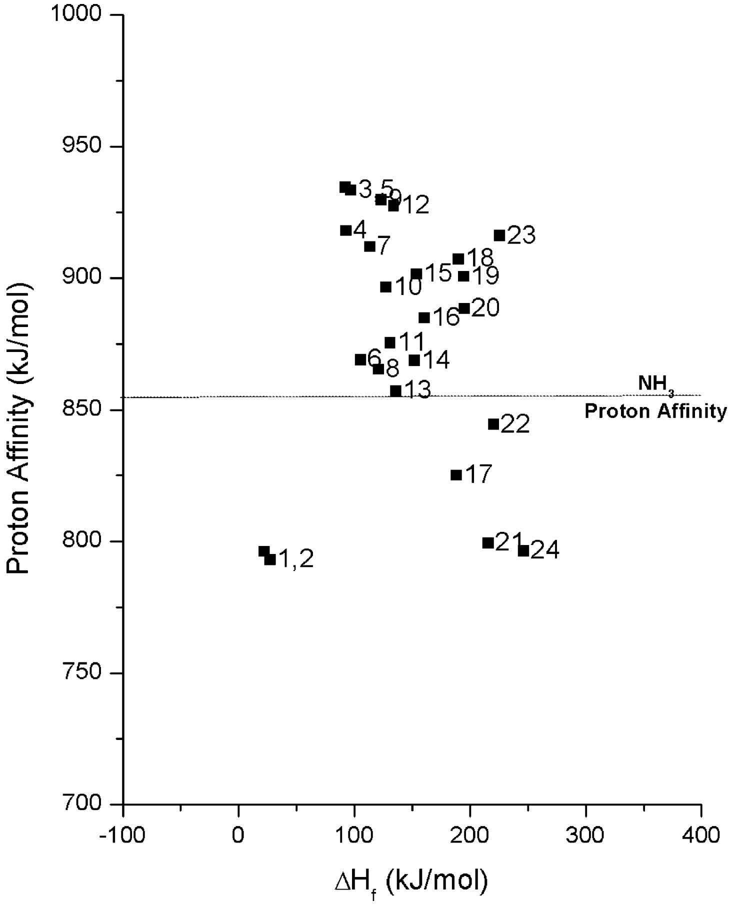


Fig. 4. Standard enthalpies of formation and proton affinities for aliphatic C_4H_7N compounds under study (see Fig. 1 for label identification).

of 854 kJ/mol, and a weak constraint on the identity for the parent neutral species is a lower enthalpy of formation.

In Figs. 4–6, the proton affinities are plotted against the enthalpies of formation for the species under study. Based on the analysis presented in the preceding paragraph, all species that have proton affinities that are less than that of NH_3 can be eliminated from consideration. In addition, using the weak constraint of lower enthalpies of formation perhaps being more favorable, the more likely candidates for the parent neutral compound of the unidentified mass 70 amu tropospheric ion should appear in the upper-left side of these plots. It is clear from Figs. 4 and 5 that for the C_4H_7N species (both aliphatic and cyclic), the proton affinity constraint is almost useless in helping to identify the mass 70 amu tropospheric ion; all but 6 of the 47 C_4H_7N compounds in this study were found to have proton affinities in excess of 854 kJ/mol. However, Fig. 6 shows that the proton affinity constraint eliminates most of the C_3H_3ON compounds (only 7 of 31 compounds considered have proton affinities greater than that of NH_3) from consideration, including the tentative assignment of isoxazole as the parent neutral species [5]. Nonetheless, the proton affinity comparison leaves quite a number of the original 78 compounds in the running as possible parent neutral species.

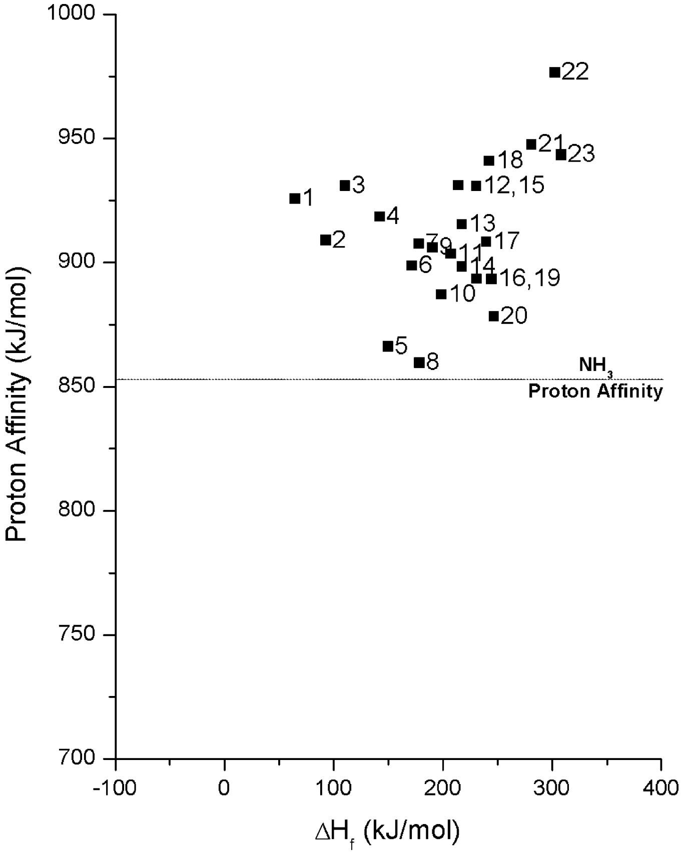


Fig. 5. Standard enthalpies of formation and proton affinities for ring C_4H_7N compounds under study (see Fig. 2 for label identification).

The next step in winnowing down the list of potential candidates was the consideration of the possible atmospheric sources of the compounds under study. The nitrogen functional groups that are present among these compounds include nitrile, amine, imine, and heterocyclic functionality. The nitrile and nitrogen heterocyclic compounds are understood to exist in the atmosphere as a result of incomplete biomass combustion.

Several nitrogen heterocyclic compounds have been observed as a result of fossil fuel combustion and in tobacco smoke, as well. The amines are largely present in the atmosphere as a result of biological decay processes [32]. An extensive literature search of the specific C_4H_7N and C_3H_3ON compounds remaining after the proton affinity consideration discussed above, turned up surprisingly few references to potential atmospheric sources of these species. In fact, the heterocyclic amine, 1-pyrroline, was the only compound for which literature reports of its potential presence in the atmosphere could be found. 1-Pyrroline has been detected as a volatile component in tobacco [33], taro [34], and wine [35], and has been found to be emitted by male locusts [36]. Our work indicates that 1-pyrroline has a very high proton affinity (925.8 kJ/mol), as well as one of the lowest enthalpies of formation for C_4H_7N compounds (72.7 kJ/mol). If the thermodynamic driving force is indeed dominant in the ion formation mechanism, neutral species with very large proton affinities, such as 1-pyrroline, should be favored. However, if the kinetic driving force is significant, relatively high concentrations of 1-pyrroline

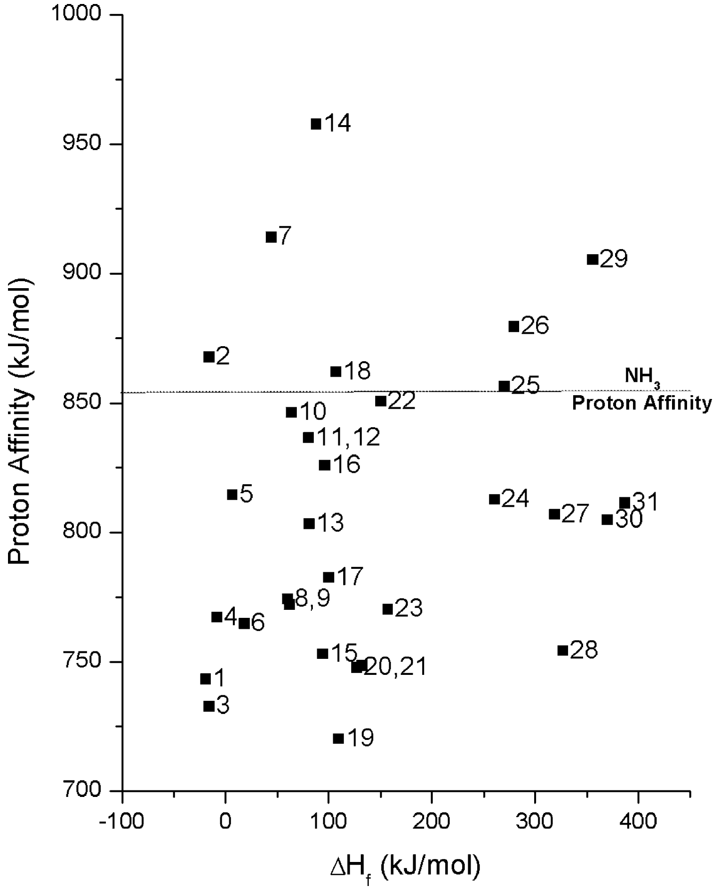


Fig. 6. Standard enthalpies of formation and proton affinities for C_3H_3ON compounds under study (see Fig. 3 for label identification).

would be required for its ion formation process to dominate. There are no available estimates for the tropospheric concentration of 1-pyrroline. In addition, kinetic data does not exist that would allow an estimate of the atmospheric lifetime of 1-pyrroline. However, because 1-pyrroline is an unsaturated hydrocarbon, it would likely have a relatively short atmospheric lifetime due to its expected high reactivity with OH [37], thus limiting its concentration in the atmosphere.

Therefore, since 1-pyrroline is the only compound of the original 78 considered for which there has been previous work indicating its possible presence in the atmosphere, and the calculated thermodynamic values presented here indicate the thermodynamic stability of the neutral species and the strong potential of this species to form a protonated ion in the troposphere, it seems that 1-pyrroline is the best candidate for the identity of the neutral parent compound to the mass 70 amu tropospheric ion. However, Eisele reports comparing the daughter ion spectrum of “pyrroline” to that of the mass 70 amu tropospheric ion, and not finding a particularly good match [5]. However, since it is not indicated which of the three pyrroline isomers was tested by Eisele (3-pyrroline appears to be the only isomer commercially available at present), and it is probable that the daughter ion spectrum would be different for each isomer, this result may not weaken the case made here for 1-pyrroline as the neutral parent compound to the mass 70 amu tropospheric ion. Nonetheless, the lack of kinetic data and atmospheric abundance information for the possible neutral precursors requires any conclusion made here concerning the identity of the mass 70 amu tropospheric ion to be somewhat uncertain. More definitive conclusions must await atmospheric detection of the neutral parent compound and laboratory measurements aimed at establishing the efficiency of ion formation processes involving 1-pyrroline.

4. Conclusions

The results of electronic structure studies aimed at determining accurate enthalpies of formation and proton affinities for a comprehensive set of C_4H_7N and C_3H_3ON compounds have been reported. The calculated thermodynamic values were rationalized in terms of the nitrogen functionality and the influence of unsaturated C–C bonding environments. Using these results, it is proposed that a previously unidentified mass 70 amu tropospheric ion is the protonated form of 1-pyrroline.

Acknowledgements

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