C_2H_5NO Isomers: from Acetamide to 1,2-Oxazetidine and Beyond

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Abstract

This work documents the properties of a number of isomers of molecular formula C_2H_5NO from the most stable, acetamide, through 1,2-oxazetidine and including even higher energy species largely of a dipolar nature. Only two of the isomers have been detected in emissions from the interstellar medium (ISM); possible further candidates are identified and the likelihood of their being detectable are considered. In general hardly any of these compounds have featured in the existing chemical literature so this work represents an important contribution extending the canon of chemical bonding which can contribute to machine-learning — providing a more exacting test of AI applications.

The presence of acetamide, $CH_3C(O)NH_2$, is the subject of current debate with no clear and obvious paths to its formation; it is shown that a 1,3[H]-transfer from (E,Z) ethanimidic acid, $CH_3C(OH){=}NH$, is feasible in spite of an energy barrier of 130 kJ mol^{-1}. It is speculated that the imidic acid can itself be formed from abundant precursors, H_2O and $CH_3C{\equiv}N$, in an acid-induced, water addition, auto-catalytic reaction on water-ice grains.

$$H_3CC{\equiv}N \xrightarrow{H_3O^+} H_3CC{\equiv}N^+H + H_2O \xrightarrow{H_2O} H_3CC(O^+H_2){=}NH \xrightarrow{H_2O} H_3CC(OH){=}NH + H_3O^+$$

Introduction

The interstellar presence of molecules with a peptide moiety, $-C(O)-NH-$, is suggestive of an extraterrestrial origin for life on Earth.[1] Acetamide, $H_3CC(O)NH_2$, is not only one of the most abundant organic molecules present in the neighbourhood of Sagittarius B2[2,3] but has also been found in comets.[4] It has been postulated to be the key precursor to more complex organic species although there are currently no obvious routes that would explain its formation in the gas-phase.[5,6] The very recent detection of propionamide, $C_2H_5CONH_2$, the next member in the homologous series, $C_nH_{2n+1}CONH_2$, suggests that peptide-like molecules might be widespread in space;[7] however, Kolesniková et al. have not confirmed this claim and could detect neither propionamide nor the unsaturated prop-2-enamide or acrylamide, $H_2C{=}CH-CONH_2$, towards Sgr B2(N).[8] Since nitriles are abundant in the ISM, Alonso et al. have speculated, that the hydrolysis of cyanoacetylene $H-C{\equiv}C-C{\equiv}N$, would lead to the formation of 2-propynamide, $H-C{\equiv}C-CONH_2$; however, the search was unsuccesful.[9]

Apart from N-methyl formamide[10] no other species with molecular formula C_2H_5NO has been found and it is therefore of interest to document those isomers and provide some key background detail of these neutral species which contain in C, H, N and O — the four basic exobiological elements.

For a wide-ranging and authoritative review of prebiotic astrochemistry and the formation of molecules of astrobiological interest in interstellar clouds and protostellar disks see Sandford et al.[11] A comprehensive study of peptide-like bond molecules, the GUAPOS project, focussed on $HNCO, HC(O)NH_2, CH_3NCO, CH_3C(O)NH_2, CH_3NHCHO, CH_3CH_2NCO,$ $NH_2C(O)NH_2, NH_2C(O)CN$ and $HOCH_2C(O)NH_2$ towards the hot core G31.41+0.31, concluding that the first five of these species which were detected are formed on grain surfaces and later released to the gas-phase by either thermal or shock-triggered desorption.[12]

Frigge et al. have calculated adiabatic ionisation energies of a number of C_2H_5NO isomers in a vacuum ultraviolet photoionisation study of the formation of N-methyl formamide in deep space.[13] But there has not been a comparable study to that of Gronowski et al. on the structure and spectroscopy of C_2HNO isomers for the C_2H_5NO isomers.[14]

However a case study[15] investigation of the possible routes to the formation of acetamide in the interstellar medium (ISM) effectively studied its constitutional isomers, creating 198 structures of which 91 were unique. Further refinement led to 53 unimolecular species[§] at the G3MP2B3 level of theory from which the authors deduced that the formation of acetamide could involve the bimolecular reactions:

$$\mathrm{H_2O + H_3C{-}C{\equiv}N \longrightarrow H_3C{-}C(O)NH_2 \longleftarrow H_3N + H_2C{=}C{=}O}$$

however they concluded that, neither these reactions, nor the isomerisations of higher-energy isomers are likely to be significant contributors to the formation of acetamide.

McCarthy and McGuire have recently summarised what is known about cyclic molecules in the interstellar medium; their review focusses on C_5 and C_6 aromatic species because cyanobenzene had been previously detected.[16] Subsequently a five membered ring has been found, 1-cyano-1,3-cyclopentadiene, its highly polar nature $\mu_a = 4.15$ D no doubt contributing to its discovery.[17] Speculations as to the presence of three-membered rings include a laboratory study of cyclopropenone[18] as well as its actual detection[19] following on from the first interstellar organic ring, cyclopropenylidene or cyclo-C_3H_2, discovered.[20] In a laboratorty study of the rotational spectrum of furan Barnum et al. have concluded that heterocyclics are peculiarly less abundant than cyclic hydrocarbons in the ISM.[21]

The search for already known isomers was conducted *here* with SciFinder® and those acyclics found are shown in Fig. 1 while cyclic species are shown in Fig. 2. The objectives of this work are two-fold: (1) to provide quality data for a series of species, some of which lie outside the normal range of molecules encountered in most chemical databases, which can then be used by machine-learning artificial intelligence procedures as standards or learning sets, and (2) to test whether any of the isomers would be easily detectable in emissions from the ISM. Note that the GDB-17 database[22] which contains upwards of 166 billion organic small molecules, with the number of 'heavy' atoms ≤ 17, and is comprised of the elements C,

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[§] None of these unfortunately were available for abstraction by Chemical Abstracts Services.

N, O, S and the halogens, only lists three such isomers, $H_3C-NH-CHO$, $H_3C-CH=N-OH$ and $H_3C-O-N=CH_2$, apart from acetamide.[23]

Theoretical Methods

Preliminary calculations used Spartan's conformer generation algorithm[24] at the ωB97X-V/6-311+G(2df,2p) level to determine the lowest lying states; those with an abundance greater than 10%, based on populations, x_i, calculated from symmetries, σ_i, and Gibbs free energies, $\Delta_f G_i^{\circ}$, and the equation:

$$x_i = \sigma_i \exp\{-\Delta_f G_i^{\circ}/RT\} / \sum_{i=1}^{n} [\sigma_i \exp\{-\Delta_f G_i^{\circ}/RT\}]$$

where (R/J mol^{-1} K^{-1}) is the molar gas constant and (T/K) is the temperature, were retained and re-optimised at B3LYP/cc-pVTZ.

High level ab initio composite methods are used to compute the atomisation energy of each species and thence the formation enthalpies. Principally Chan and Radom's W3X-L protocol[25] is employed which is based on B3LYP/cc-pVTZ+d geometries and frequencies. The latter are scaled by 0.9886, 0.9926 and 0.9970 to account for the zero-point energy, the thermal corrections to the enthalpy and entropy respectively. Energetics are computed by a combination of coupled-cluster determinations, CCSD(T) and CCSD(T)-F12b, extrapolated to the complete basis set limit (CBS) with aug-cc-pVnZ basis sets up to aug-cc-pVQZ. Core valence correlation and scalar relativistic calculations were performed at the CCSD(T)/cc-pCVTZ level using non-relativistic frozen-core and and all-electron Douglas-Kroll-Hess methods and MP2 and CCSD(T) energies. The above signifies the W2X component of the W3X-L method computed by the Molpro[26] code; the final steps involve post-CCSD(T) effects up to CCSDT(Q) using the multi-reference application MRCC.[27,28]

In some cases the computationally less-demanding WMS method has been used, also centered on B3LYP/cc-pVTZ+d geometries and not on those originally specified by the WMS

(a) 1-Amino-ethenol

(b) 2-Amino-ethenol

(c) 2-Imino-ethanol

(d) Acetamide

(e) Amino-acetaldehyde

(f) Ethanimidic-acid

(g) Methylene-amino-methanol

(h) Methyl formimidate

(i) N-hydroxy-ethenamine

(j) Nitrosoethane

(k) N-methyl-formamide

(l) N-methylene-N-oxide-methanamine

(m) O-ethenyl-hydroxylamine

(n) O-methyl-oxime-formaldehyde

(o) Oxime-acetaldehyde

(p) 2-Hydroxy-ethyl-imidogen

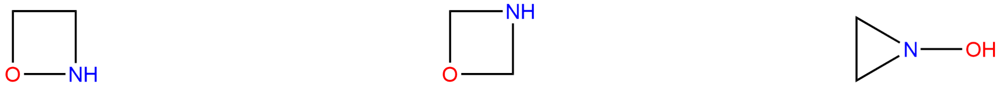
(q) Ethoxy-imidogen

(r) Methoxy-methyl-imidogen

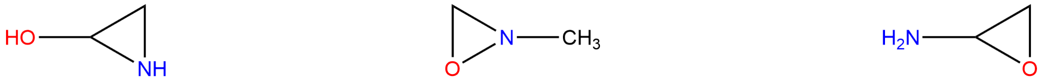
(s) Hydroxy-methylamino carbene

(t) Methoxy-amino carbene

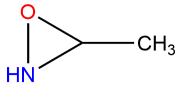
Figure 1: Structures of acyclic species



(a) 1,2-Oxazetidine (b) 1,3-Oxazetidine (c) 1-Hydroxy-aziridine



(d) 2-Aziridinol (e) 2-Methyl-oxaziridine (f) 2-Oxiranamine



(g) 3-Methyl-oxaziridine

Figure 2: Structures of cyclic species

developers.[29] It has been recently shown[30] that this functional, B3LYP, has an excellent performance relative to W1-F12//CCSD(T)/CBS and consequently W1-F12 energies computed from the functional geometry, that is W-F12//B3LYP/Def2-TZVPP, exhibit a root-mean-square deviation of only 0.29 kJ mol^{-1} and that using a cc-pVTZ+d basis set leads to even better, if unspecified, results. Since only CHNO species are considered *here* cc-pVTZ+d is equivalent to cc-pVTZ.

The WMS composite method can be summarised as (1) the achievement of CCSD(T)/CBS valence correlation energy but via the CCSD(T)-F12b method with only double-ζ and triple-ζ basis sets, (2) parametrisation to extrapolate the higher-order valence correlation energy from MP2/CBS, CCSD/CBS and CCSD(T)/CBS components and (3) low-cost procedures for inner-shell contributions and scalar relativistic corrections.[29]

Ionisation energies were calculated from G4 computations[31] of the neutral molecule and the associated cation; in addition formation enthalpies derived from G4 atomisation values were obtained.[32]

The applications Gaussian and ChemCraft were variously employed to carry out the calculations and to manipulate the results.[33,34]

Results and Discussion

Computational results for the different categories of molecules under consideration are grouped as follows: firstly, acyclics whose structures are shown in Fig. 1, secondly cyclics in Fig. 2 and thirdly dipolar species with untypical valences . The first two sets can be discussed on an individual basis but the dipolar species are simply illustrated in Fig. 17 and their basic data listed in Table 5.

An extensive comparison of the properties of those species presented *here* with the literature is not possible except for adiabatic ionisation energies; this comparison is discussed below on page 26 and shown in Table 4.

Arising out of the results there is a discussion of the possible routes by which the most stable isomers, acetamide and N-methyl formamide, might be formed in the ISM on page 35 with the intention of identifying other suitable candidates for detection and their connection to either acetamide or N-methyl formamide.

1-Amino-ethenol

Has been considered as an intermediate in a quantum chemical study of the ammonolysis of ketene, $H_2C{=}C{=}O + NH_3 \longrightarrow H_2C{=}C(NH_2)OH$, which leads ultimately to acetamide.[35] They place this species at -9.0 kcal mol^{-1} relative to ketene[36] + ammonia[36] from CCSD(T)/CBS//MP2/aug-cc-pVTZ calculations, which implies a formation enthalpy of $(-45.35 \pm 0.12) + (-38.564 \pm 0.029) + (-37.66) = -121.6$ kJ mol^{-1}. This is in excellent agreement with that computed directly *here* of -121.5 kJ mol^{-1} as indeed are the geometries cf. C=C 134.2, 133.9 pm; C=O 136.5, 136.6 pm and C=N 138.5, 138.4 pm and CCOH $-3.3°$, $+3.3°$. A second *syn* conformer lies 4.5 kJ mol^{-1} above with $\angle$CCOH $= -150.2°$.

The compound was recently synthesised via the flash vacuum pyrolysis of malonamic acid and characterised spectroscopically, by trapping in an argon matrix at 10 K, as part of a study of interstellar presence of pre-biotic molecules.[37] The authors show via coupled cluster computations at the AE-CCSD(T)/cc-pVTZ level of theory reaction energy profiles of

1,3[H]-transfers linking *anti* 1-amino ethenol and (*Z,E*) ethanimidic acid, and, *syn* 1-amino ethenol and (*Z,Z*) ethanimidic acid, Fig. 3.

2-Amino-ethenol *Z*

The *Z* conformer is only mentioned once in the literature where it is postulated as an intermediate in the atmospheric chemical reaction between the solvent monoethanolamine, $H_2NCH_2CH_2OH$, and the OH radical; that study was prompted by the possible large-scale use of the solvent in post-combustion carbon dioxide capture technologies.[38]

The ground state $^1A'$ of C_s symmetry has $\angle HOCC = 0°$ and $\angle CCNH = \pm 119.9°$; relaxed potential energy scans are compromised by through-space interactions between the OH and NH_2 groups — it is considerably more stable than the *E* conformer by some 16 kJ mol^{-1}.

2-Amino-ethenol *E*

The lowest energy rotamer of the *E* conformers has a CCOH dihedral of ca. 0°; scans about the C-O and the C-N bonds are well-behaved while the more symmetric C_s state with $\angle HOCC = 0.0°$ and $\angle CCNH = \pm 120.4°$ lies 1.7 kJ mol^{-1} higher with $\Delta_f H^{\circ}(0\ K) = -75.6$ kJ mol^{-1}.

These amino ethenols or enamines are tautomers of the imino ethanols or imines below; Lin et al. showed[39] that the enamine $HOCH{=}CH{-}NH_2$ or 2-amino-ethenol-*E* lies 18.3 kJ mol^{-1} higher in energy than the corresponding imine, $HOCH_2CH{=}NH$, 2-imino-ethanol-*Z*; the corresponding numbers found *here*, Table 2, are $|(-97.6) - (-77.3)| = 20.3$ kJ mol^{-1}.

2-Imino-ethanol *Z*

The lowest energy conformer can be categorised, based on HNCH / CCOH dihedrals, as (*Z,Z*) with C_s symmetry overall. Rotation about the C–O bond yields the (*Z,E*) which is at +27.5 kJ mol^{-1}.

2-Imino-ethanol *E*

The lowest energy conformer is best described as (∼*E,gauche*) according to NCCO / CCOH dihedrals of −4.3° and −75.1°; the more symmetric C_s state is very close at +0.7 kJ mol^{-1}. Two other conformers, variously (*g,g*), lie within +11 kJ mol^{-1}.

In a study of dissociation of amide bonds in peptides Paizs *et al.* show that the neutral *E* imine is 11.7 kJ mol^{-1} more stable (electronic energies uncorrected for ZPEs) than the *Z*.[41] A conclusion which is reinforced here with a zero-point corrected electronic energy difference of 10.2 kJ mol^{-1}.

2-Imino-ethanol, of an unspecific sterochemistry, crops up as an intermediate in flow experiments synthesising 2-aminooxazole — a key heterocycle leading to nucleotides — from possible prebiotic feedstocks under conditions thought to have existed on an early Earth.[42]

It is also an end product in a G3SX study of the atmospheric chemistry of monoethanolamine, or 2-amino ethanol, which is a widely used solvent for so-called 'carbon capture'. Specifically da Silva uses quantum chemical calculations and master equation kinetic modelling to explore the reaction between the $H_2N\dot{C}HCH_2OH$ radical and O_2 in which the imine, 2-amino ethanol, and the hydroperoxyl radical are formed.[40]

Acetamide

The most stable of all the species with molecular formula C_2H_5NO, acetamide is also very well characterised with a formation enthalpy at 298.15 K determined by combustion calorimetry[43] of -238.33 ± 0.78 kJ mol^{-1}. At 0 K the Thermodynamics Research Centre[44] recommends −221.0 kJ mol^{-1}. The W3X-L results shown in Table 2 are in substantial agreement with $\Delta_f H^{\circ} = -221.7$ kJ mol^{-1} at 0 K and −237.1 kJ mol^{-1} at 298.15 K as indeed is WMS.

It has been detected in emission and absorption in a star forming region near the Galactic centre together with its parent formamide, $HCONH_2$.[45] The GUAPOS project indicated its presence, outside the Galactic centre, in the hot molecular cloud G31 and speculated that acetamide and more generally −C(O)NH− species are prevalent in massive and clustered star-forming regions akin to that in which our Sun was formed.[12]

The very low barrier to internal rotation of the methyl group of ca. 24 cm^{-1} means that syn, anti *and* perpendicular conformations have been found depending on the level of theory and basis set.[46] Here the conformation is best declared as *syn*. The availability of multiple low-lying rotamers makes the rotational spectrum very complex[46] and has also hindered computations of its thermochemistry such as entropy and heat capacity. Only a very recent determination[47] exists for the isobaric heat capacity, $C_P^{\circ} = 73.38$ and entropy, $S^{\circ} = 274.9$ J K^{-1} mol^{-1} at 1 atm and 298.15 K; tests indicate that the results are strongly dependent on the treatment applied with the best values obtained *here* of $S^{\circ} = 312.2$ and $C_P^{\circ} = 74.27$ J K^{-1} mol^{-1} when the two vibrational modes, $\bar{\nu}_1 = 27.4$ and $\bar{\nu}_4 = 503.7$ cm^{-1} are replaced by a methyl torsion and a $H_2N{-}C$ torsion respectively, with all the other frequencies anharmonics. The H_2NX 'umbrella' mode at $\bar{\nu}_2 = 146.3$ cm^{-1} remains as a stumbling block to precise evaluation.

An adiabatic ionisation energy of 9.71±0.02 eV has been determined by VUV photoionisation experiments[48] using synchrotron and photoelectron/photoion coincidence spectroscopy, in excellent agreement with a G4 computed value 9.70 eV, Table 4.

Amino-acetaldehyde

Balabin showed, from focal-point analysis and *ab initio* limit computations up to CCSD(T)/CBS, that this keto form is 31.4 ± 1.8 kJ mol^{-1} more stable than the enol form, in this case, 2-amino-ethenol.[49] The difference found *here* is $|(-115.2) - (-77.3)| = 37.9$ kJ mol^{-1} but this is for the most stable conformer of amino-acetaldehyde whose OCCN dihedral of 0° and CCNH dihedrals of ±57.7° results in C_s symmetry and not the implied structure in the Balabin work (OCCN $= -150.0°$ and CCNH $= 79.8°, -160.8°$) which is 7.3 kJ mol^{-1} *higher* in energy. The directly comparable results are in good agreement, viz. $37.9 - 7.3 = 30.6$ vs 31.4 ± 1.8 kJ mol^{-1}.

Ethanimidic acid

The dominant conformer is the (*E*,*Z*) labelled according to the OCNH/HOCN dihedrals with the (*Z*,*Z*) at +11.9 kJ mol^{-1}, the (*Z*,*E*) at +14.3 kJ mol^{-1}, and the (*E*,*E*) at +25.3 kJ mol^{-1} in all cases the molecules exhibit C_s symmetry, Fig. 3.

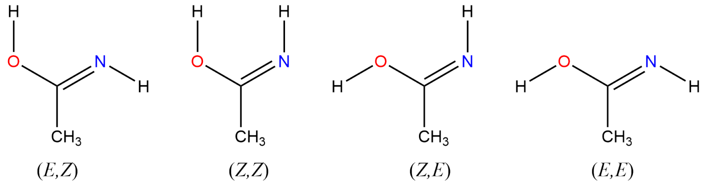


Figure 3: Ethanimidic acid conformers

Seasholtz et al. studied the energetics of imino compounds at the G2 level of theory including acetimidic or ethanimidic acid.[50] They report $\Delta_f H^{\circ}$ of −175.3 and −191.2 kJ mol^{-1} at 0 K and 298.15 K, respectively, and a methyl rotor barrier of 5.0 kJ mol^{-1} for 'the most stable', but unspecified, conformer. WMS, W2X and W3X-L based values are $\Delta_f H^{\circ}(0\ K) = -173.1, -174.6, -174.7$ kJ mol^{-1} and a 298.15 K of $-190.5, -192.0, -192.1$ kJ mol^{-1} as found here for the (*E*,*Z*).

Here WMS, W2X and W3X-L 0 K values are $-159.1, -160.4$ and -160.3 kJ mol^{-1} as well as a barrier of 6.8 kJ mol^{-1} is reported for the (*Z*,*E*).

The literature value[13] for the ionisation energy of ethanimidic acid is given as 9.65 eV, Table 4, as against a computed value of 9.72 eV for the (*E*,*Z*) but the former probably refers to the (*Z*,*E*) conformer for which we compute a more agreeable 9.62 eV.

Ethanimidic acids appear as intermediates in the dissociation of a radical formed by femtosecond electron transfer to the stable cation formed by O-protonation of N-methylacetamide, Fig. 4 shows formation of the (*E*,*Z*) conformer. The objective of the study was to investigate simpler models of the process known as electron capture dissociation with implications for research into medical aspects of ageing, radiation damage and oxidative stress.[51]

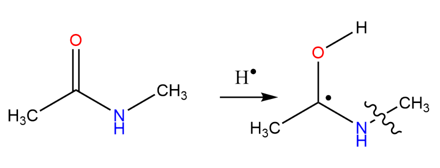


Figure 4: 1-Hydroxy-1-(N-methyl)aminoethyl radical dissociation

Methyleneamino-methanol

The lowest conformer, #1, has OCNC and HOCN dihedrals of 1.7° and 79.5° respectively, #2 has C_s symmetry at +4.0 kJ mol^{-1} and another, #3, with 130.6°/47.9° also at +4.0 kJ mol^{-1}. The conformer tabulated by Frigge et al. is probably closest to #3, which is described as 165 kJ mol^{-1} less stable than acetamide and with an ionisation energy of 9.18 eV.[13] The comparable values obtained *here* for the lowest conformer are 149 kJ mol^{-1} and 9.39 eV — clearly not a valid comparison.

Although methyleneamino methanol is listed by Scifinder ® it has zero references associated with it (14-Aug-2021) thus omitting the Frigge work altogether.

Methyl formimidate

The methyl ester of methanimidic acid or O-methylformimidate exists in E and Z stereoisomers and anti- and synperiplanar conformations of C_s symmetry, Fig. 5, as delineated by Lumbroso and Papparlardo in early SCF-MO/4-31G calculations who found that the (E, ap) form is the most stable.[52]

A conclusion which is reinforced by G4 calculations which ranks their $\Delta_f H^{\circ}(0\ \mathrm{K})$ as follows:

(Z, ap) : (Z, sp) : (E, ap) : (E, sp) = −93.1: −89.3 : −105.3 : −83.2 kJ mol^{-1}

In absolute terms there is good agreement for the (E, ap) for which WMS predicts −104.9 kJ mol^{-1} at 0 K. Note that the total dipole moment, $\langle\mu\rangle = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$, varies considerably from a low of 0.67 D for the (E, ap) to a high of 3.59 D for the (E, sp) conformer.

The rotational barriers about the N−C−O−C dihedral are quite high viz (E, ap)→(E,

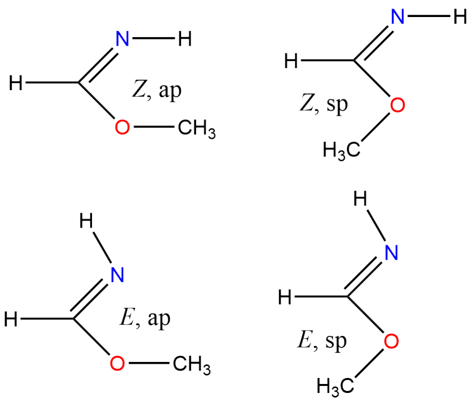


Figure 5: *E,Z* stereoisomers and syn- and periplanar conformations

sp) = 44.7 and (Z, ap)→(Z, sp) = 32.2 kJ mol^{-1} whereas the methyl rotors are typically much lower at 6–10 kJ mol^{-1}.

N-hydroxy-ethenamine

The ground state has effectively a cis/gauche conformation of CCNO/CNOH dihedrals of $-18.4°$ / 116.4 , a change in CNOH to $-46.7°$ results in a conformer at +6 kJ mol^{-1} whilst gauche/gauche of 140.0° / 124.6° lies 26 kJ mol^{-1} above . Rotation about the C–N bond faces a barrier of 36.6 kJ mol^{-1} whilst a relaxed potential energy scan about the N–O bond has a barrier of 21.1 kJ mol^{-1} to the next low-lying conformer.

Nitroso-ethane

The lowest energy conformer has a *cis* or *syn* arrangement with C_s symmetry with two *gauche* forms, $\angle$CCNO = ±123.4°, lying very close at ≈ 2 kJ mol^{-1}. The difference between *syn* and *anti* forms (described as *anti* but in reality *gauche*) is slight, ranging from 1–3 kJ mol^{-1} according to Fu and co-workers.[53]

Detailed explorations of the microwave spectrum and the potential functions have been carried out by Cox et al.[54,55] In careful relative intensity measurements they determined a *cis/gauche* zero-point energy difference of 175 ± 35 cm^{-1} or 2.1 ± 0.4 kJ mol^{-1}. This is in excellent agreement with WMS calculations which yield $\Delta\{\Delta_f H^{\circleddash}(0\ K)|syn - gauche|\} =$

$|58.72 - 60.79| = 2.07$ kJ mol^{-1}.

Relaxed potential energy scans of the methyl and ethyl rotors have barriers of 9.4 and 8.1 kJ mol^{-1} respectively for the ground state conformer.

N-methylene-N-oxide-methanamine

The ground state $^1A'$ of N-methylene-N-oxide-methanamine or N-methylnitrone has C_s symmetry; the three-fold methyl rotor has a barrier of 6.9 kJ mol^{-1}. Łukomska et al. discuss the nature of the bonding in this compound and show that the N−O bond in this acyclic N-oxide should be considered as a single dative bond $N^{\oplus}\rightarrow O^{\ominus}$ with only a negligible contribution from a double bond.[56] Furthermore they show that although primarily a single bond the NO bond is significantly shorter at 1.266 Å (*here* 1.262 Å) and stronger at 556 kJ mol^{-1} than other cyclic N-oxides. Komaroni et al. argue that the electronic structures of the nitrones cannot be represented by one well-defined Lewis-type structure but instead are a mixture of the zwitterionic and the hypervalent.[57]

Other nitrones are possible, for example a C-methyl nitrone rather than an N-methyl, Fig. 6, with *E* and *Z* conformers. The order of stability is $Z > E > H_3CN(O){=}CH_2$ which parallels that for the ethanimines $HN{=}CHCH_3$ and N-methylene methanime $H_3CN{=}CH_2$. Boyd and Boyd carried out theoretical studies of the addition to, and abstraction from, by methyl radicals from a series of nitrones[58] but otherwise they rarely feature in the chemical literature.

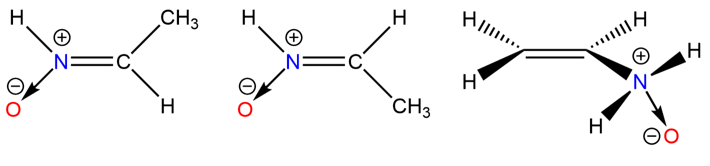


Figure 6: (*E*) and (*Z*) C-methyl nitrones and vinyl nitrone

Here both conformers share C_s symmetry and similar N–O bondlengths of 1.263 Å and 1.266 Å respectively, with the *Z* 11.1 kJ mol^{-1} more stable. A significant difference is that the methyl rotor barrier slumps to 1.4 kJ mol^{-1} in the *Z* from 7.0 kJ mol^{-1} for the *E*.

Yet another nitrone is feasible as found by Foo et al.;[15] this vinyl-nitrone, $H_2C{=}CHN(\rightarrow O)H_2$, has a significantly longer N–O bondlength at 1.361 Å, not unexpectedly a large dipole moment of $\langle\mu\rangle = 4.776$ D and $\Delta_f H^{\circ}(0\ \mathrm{K}) = 170.9 \pm 2.6$ kJ mol^{-1} estimated from multi-composite atomisation computations, Fig. 6.

N-methyl-formamide

On the basis of a molecular line survey at 84.1–114.4 GHz N-methylformamide has been tentatively detected[10] by Belloche and co-workers as well as more recently and confidently towards Sgr B2(N) and in the star-forming region NGC 63341.[6,61]

Terrestrially this very well known species has a ground state of $^1A'$ and C_s symmetry. The conformer with *cis* Hs, technically this is the (Z) conformer, is some 5.5 kJ mol^{-1} more stable than that with *trans* Hs or (E) conformer in agreement with earlier work[59] and with a study of nitrogen species by a series of composite methods[60] where the difference was reported as 5.38 ± 0.8 kJ mol^{-1} at 298.15 K.

Leach et al. quote[62] a value of ΔH° of -1.938 ± 0.031 eV and reference the NIST Chemistry WebBook as of June 2005 but this link no longer exists; their photoionisation mass spectrometric study yielded an adiabatic ionisation energy of 9.55 ± 0.04 eV, substantially different from previous determinations. The WebBook itself quotes 9.83 ± 0.04 eV which is in accord with all recent theoretical determinations, viz. *this work* 9.79 eV, Frigge et al.[13] 9.80 eV.

N-methyl-methanimidic acid

Imidic acids are tautomers of amides and are isomeric to oximes. This particular imidic acid, also known as N-methyl formimidimic acid, which currently is not catalogued by SciFinder® (25-July-2021), is a tautomer of N-methyl-formamide and is closely related to O-methyl-oxime-formaldehyde, Fig. 7.

An extensive theoretical study of the parent imidic acid $HN{=}C(OH)H$ was carried out

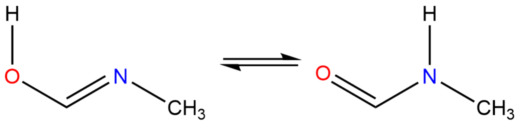


Figure 7: N-methyl-methanimidic acid, (*E*, antiperiplanar)

in order to understand the relationship between its tautomers.[63] While Maier and Endres have demonstrated the formation of imidic acid during the photolysis of formamide in an argon matrix with the (*s*-*Z*)-(*E*) being formed preferentially.[64] The same applies here where the (*Z*,*E*) conformer is preferred to the (*E*,*E*), (*E*,*Z*) and (*Z*,*Z*) at +16.9, +18.3 and +20.4 kJ mol^{-1}, respectively, where the first refers to orientation about the CN=CO bond and the second about the NC−OH bond, Fig. 8.

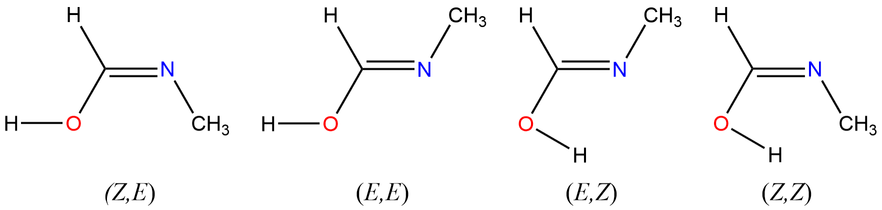


Figure 8: N-methyl formimidic acids

Crespo-Otero and co-workers[65] show that the (*s*,*Z*)-(*E*) conformer, that is ∠NCOH = 0° is 21.6 kJmol more stable than the (*s*,*E*)-(*E*) conformer, ∠NCOH = 180°.

O-ethenyl-hydroxylamine

There are three main conformers to consider, all have C_s symmetry; the lowest has a CCON *trans* configuration with CONH dihedrals of ±124.9° while the two have a CCON *cis* arrangement with ∠CONH = ±124.9° and lies very close in energy ≈ 0.1 kJ mol^{-1} or with ±56.4° at +6.1 kJ mol^{-1} — there is almost nothing known about this compound.

O-methyl-oxime-formadehyde

Both conformers are of C_s symmetry and electronic state ^{1}A′ with the *E* some 23.9 kJ mol^{-1} more stable than the *Z*. Relaxed potential energy scans of methyl group show a typical three-fold symmetry with a barrier of 19.1 kJ mol^{-1}; rotation about O−N faces a barrier of 41.1 kJ mol^{-1} before interconverting to the Z at 22.4 kJ mol^{-1}.

Kalinowski et al. have studied the ozonolysis of O-methyloxime as a means to understanding the stability of Crigee intermediates; their starting point is the higher energy Z conformer.[66,67]

Oxime-acetaldehyde-*E*

Aldoximes have the general formula RHC=NOH and for R=CH_3 exists in E and Z forms. A matrix isolation FTIR and molecular orbital study classified the structures according to rotation about the single bonds C–C and N–O as *cis* or *trans* about HCCN and CNOH; thus *cEc* and *cEt*, and *tZc* and *tZt*. The global minimum corresponds to *cEt* with the *tZt* only 2.6 kJ mol^{-1} higher.[68]

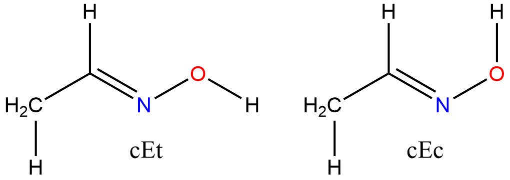


Figure 9: Acetaloximes, E

A number of composite methods, G2, G3, G3B3 and G3MP2B3, was used to calculate the enthalpies of formation of substituted hydroxylamines and oximes[69] including acetaloxime with $\Delta_f H^{\ominus}(298.15\mathrm{K}) = -21.9 \rightarrow -22.5$ kJ mol^{-1} which agree with an earlier determination[70] of -22.55 ± 0.29 kJ mol^{-1}; the corresponding value found *here* is -22.1 kJ mol^{-1}, Table 2.

Hosoi and co-workers have observed the microwave spectra of six isotopic species of (E) and (Z) acetaldehyde oximes or acetaloximes.[71] For the E they determined rotational constants of $45,453 \pm 560$, $4,237.665 \pm 21$ and $3,973.807 \pm 21$ MHz and an average barrier height for the methyl rotor of 7.88 ± 0.20 kJ mol^{-1}. The comparable numbers calculated *here* of $A_e = 46,620$, $B_e = 4,238$ and $C_e = 3,980$ MHz are probably uncertain to the extent of ± 1%.[72]

Oxime-acetaldehyde-*Z*

For the Z Hosoi et al. determined rotational constants of $17,215 \pm 18$, $6,626.48 \pm 40$ and $4,920.70 \pm 34$ MHz and an average barrier height for the methyl rotor of 1.65 ± 0.08 kJ mol^{-1}. They attribute the drastically lower barrier to steric repulsion between the methyl and hydroxyl groups, a conclusion with which we concur as the methyl rotor barrier slumps from $8.1 \rightarrow 0.2$ kJ mol^{-1}.

Here rotational constants (MHz) of $A_e = 17,450$, $B_e = 6,580$ and $C_e = 4,920$ are computed. Note that for both E and Z stereoisomers Hosoi et al. did not directly measure either the rotational constant A or the moment of inertia, $I_a = h/(8\pi^2 cA)$, but instead estimated the latter from the approximate relation $I_a \approx I_c - I_b$.

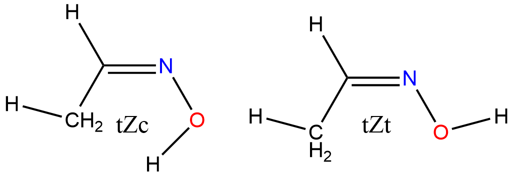


Figure 10: Acetaloximes, Z

Carbenes

Hydroxy(methylamino) carbene

The existence of hydroxy(methylamino) carbene was demonstrated by gas-phase experiments in which one-electron reduction of radical cations was followed by neutralisation-reionisation.[73] Thus, $H_3C{-}N{=}C(H){-}OH$, N-methyl-methanimidic acid, and $H_3C{-}NH{-}\ddot{C}{-}OH$ were established.

The lowest state corresponds to a *trans/trans* arrangement for HOCN and OCNC dihedrals with a *cis/trans* structure at +19.7 kJ mol^{-1}; both singlet states are of C_s symmetry — the triplet is at a very much higher energy.

Very recently a *trans* aminohydroxymethylene carbene has been synthesised, $H_2N-\ddot{C}-OH$, by pyrolysis of oxalic acid monoamide and trapping in solid argon.[74] IR spectra at 3 K together with a computed anharmonic spectrum at B3LYP/6-311++G(3df,3pd) enabled the identification. Geometrically, $\angle O\ddot{C}N = 107.8°$, $d(O-\ddot{C}) = 1.347$ Å and $d(\ddot{C}-N) = 1.322$ Å; these compare well with hydroxy(methylamino) viz. 107.7°, 1.356 Å and 1.319 Å.

Methoxy(amino) carbene

In agreement with Alkorta and Elguero[75] the singlet is considerably more stable than the triplet carbene — at the G4 level by 311.9 kJ mol^{-1}; an index name for this species, $H_2N-\ddot{C}-O-CH_3$, is as yet unassigned by SciFinder® (15/06/2021).

The lowest conformer has a *trans* COCN structure with the *cis* conformer at +28.9 kJ mol^{-1}, both have C_s symmetry, Fig. 11.

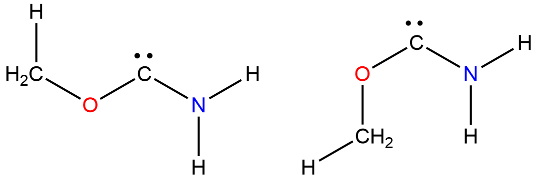


Figure 11: Methoxy(amino) carbenes

Other carbenes

A number of variants are feasible all of which are considerably less stable than the two carbenes considered above but still more stable than cyclopropenylidene or indeed methylene. These higher energy isomers, some of which are derived from the structural work of Foo and colleagues,[15] are ranked in order of increasing formation enthalpy in Table 1.

Table 1: Other carbenes: / kJ mol^{-1}

Species	$\Delta_f H^{\circ}$(0 K)	$\Delta_f H^{\circ}$(298.15 K)	$\langle\mu\rangle$ / D
$H_2N-\ddot{C}-CH_2-OH$	39.3	23.7	2.14
$H-\ddot{C}-NH-CH_2OH$	90.0	74.9	4.13
$HO-\ddot{C}-CH_2-NH_2$	116.7	102.2	1.96
$H-\ddot{C}-O-CH_2-NH_2$	132.6	117.2	1.43
$H_3C-\ddot{C}-NH-OH$	165.9	152.3	1.57
$H-\ddot{C}-N(CH_3)-OH$	182.3	167.1	1.49
$H-\ddot{C}-O-NH-CH_3$	278.4	263.0	1.99

Nitrenes

2-Hydroxy-ethyl-imidogen

The lowest triplet state has dihedrals HOCC and OCCN of −64.2° and +66.9° respectively with the more symmetric C_s at +4.5 kJ mol^{-1}. In a computational study of the reaction of triplet nitrenes with oxygen Liu *et al.* found[76] that 2-hydroxy-ethyl imidogen, $HOCH_2CH_2^3N$, is some 41.4 kJ mol^{-1} more stable than ethoxy imidogen, $CH_3CH_2O^3N$. This is in good agreement with the value computed here of (206.6 – 164.1) = 42.5 kJ mol^{-1}, Table 2.

Ethoxy-imidogen

The triplet state is considerably more stable than the singlet in agreement with earlier work of the Hadad group;[76] the ground state has an NOCC dihedral of 180° and C_s symmetry and is accompanied by two close-lying conformers, with NOCC dihedrals of ±75°, generated by relaxed PE scans with barriers of 3.7 kJ mol^{-1}, whereas the equivalent scan for the singlet state is accompanied by dissociation.

Methoxy-methyl-imidogen

MNDO investigations of the 1,2-rearrangement of singlet carbenes and nitrenes by Frenking and Schmidt included $CH_3OCH_2-\ddot{N} \longrightarrow CH_3OCH{=}NH$.[77]

The ground triplet state is not the obvious *trans*, of C_s symmetry, but a *gauche* $\angle$COCN =

$-72.3°$ which lies 5.3 kJ mol^{-1} lower.

Table 2: Results for acyclics / kJ mol^{-1}

Species	$\Delta_f H^{\ominus}$(0 K)	$\Delta_f H^{\ominus}$(298.15 K)	$\langle\mu\rangle$ / D
1-Amino-ethenol	−121.5	−138.3	1.069
2-Amino-ethenol *Z*	−94.9	−112.2	2.190
2-Amino-ethenol *E*	−77.3	−93.5	1.602
2-Imino-ethanol *E*	−87.4	−103.6	3.375
2-Imino-ethanol *Z*	−97.6	−115.2	3.073
Acetamide	−221.7	−237.1	3.818
Amino-acetaldehyde	−115.2	−121.7	1.624
Ethanimidic acid *E,Z*	−174.7	−192.1	1.503
Methylene-amino-methanol	−69.7	−77.1	1.515
Methyl formimidate (*E*, ap)	−104.9	−122.3	0.671
N-hydroxy-ethenamine	57.0	40.0	1.320
Nitroso-ethane	58.8	42.1	2.471
N-methyl-formamide *cis*	−172.2	−188.6	3.901
N-methyl-methanimidic acid	−124.6	−141.7	0.738
N-methyl-nitrone	61.5	43.7	3.567
C-methyl-nitrone *Z*	37.2	22.3	3.500
C-methyl-nitrone *E*	48.3	33.6	4.124
Vinyl nitrone	170.9	154.7	4.776
O-ethenyl-hydroxylamine	79.0	61.7	1.895
O-methyl-oxime-formadehyde *E*	51.8	35.4	0.265
Oxime-acetaldehyde *cEt*	−5.6	−22.1	0.725
Oxime-acetaldehyde *tZt*	−5.0	−21.3	0.694
Carbenes & Nitrenes			
Amino-hydroxymethyl-carbene ^{1}A$'$	39.3	23.7	2.431
Hydroxy-methylamino-carbene ^{1}A$'$	−18.3	−33.6	1.490
Methoxy-amino-carbene ^{1}A$'$	4.6	−11.5	1.472
2-Hydroxy-ethyl-imidogen ^{3}A	164.1	147.9	1.451
Ethoxy-imidogen ^{3}A$''$	206.6	190.5	2.927
Methoxy-methyl-imidogen ^{3}A	211.2	194.9	1.847

Cyclics

1,2-Oxazetidine

In a study of conventional ring strain energies in oxadiazetidines Benton and Magers showed that 1,2-oxazetidine is much less strained than all of the six systems examined in spite of the fact that its total electronic energy is some 121–16 kJ mol^{-1} higher than 1,3-oxazetidine.[78] Galván and co-workers have shown that in contrast to 1,2-dioxetane, 1,2-oxazetidine cannot undergo chemiexcitation and subsequent chemiluminescence.[79]

1,3-Oxazetidine

As alluded to above this isomer of C_s symmetry and state ^{1}A$'$, is 119.6 kJ mol^{-1} more stable than the 1,2-oxazetidine, Table 3. It is noticeably less 'buckled' than the 1,2-isomer.

Even a comprehensive treatise on heterocyclic chemistry which deals specifically with four-membered rings with one oxygen and one nitrogen atom has remarkably little to say about oxazetidines.[80]

1-Hydroxy-aziridine

This symmetric system, C_s and ^{1}A$'$, exists in two forms with the 180° some 22.25 kJ mol^{-1} more stable than the 0° at the G4 level where the dihedral angle is defined by H–O–N to the C–C midpoint. A relaxed potential energy scan faces a barrier of 23.6 kJ mol^{-1} leading to the 0° conformer at 22.0 kJ mol^{-1}.

2-Aziridinol

This chiral molecule, 2-hydroxyaziridine, is mainly, 72.6%, in the *trans* form with opposed OH and NH groups and $\angle$NCOH $= 8.5°$, *cis* or same side groups lie at +4.5 kJ mol^{-1} with $\angle$NCOH $= -88.7°$ and contribute 18.6% while a further *cis* conformer is at +7.2 kJ mol^{-1} or 4.4% and differs from the previous by a NCOH dihedral of +156.8°.

The high-symmetry, C_s and ^{1}A$'$, nitrone-type molecule[15] shown in Fig. 12, $\angle$ONH $=$ 116.4°, d(O−N) = 1.318 Å and d(N−H) = 1.024 Å; has a large dipole moment, $\langle\mu\rangle = 4.869$ D but also a very large formation enthalpy of 195.7 kJ mol^{-1} (178.0 at 298.15 K).

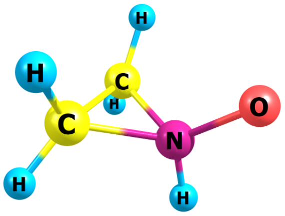


Figure 12: Aziridine N-oxide

2-Methyl-oxaziridine

This N-methyl substituted oxaziridine has a ground state with an unusually long O–N bond[81] of 1.498 Å; the methyl rotor barrier of 12.4 kJ mol^{-1} is unexceptional.

Apart from two articles concerned with the calculation of optical rotation for this chiral molecule there is little else in the literature.[82,83]

2-Oxiranamine

The lowest energy conformer corresponds to OCNH dihedrals of $+80°/-41°$ while scans about the C−N bond indicate two others at +12.6 kJ mol^{-1} with $\angle$OCNH $= +96°/-143°$ and +12.3 kJ mol^{-1} with $-56°/-179°$.

In a fascinating article Ellinger and others address the question of chirality in the interstellar medium.[84] Arguing from the fact that currently the only chiral species detected is propylene oxide, c-(H_2COCH)−CH_3, they adduce that successful detection requires:

- a 'rigid molecule' — leading to a rotational spectrum of least complexity.
- a significant dipole moment — probably of the order of 2 Debye.
- a high abundance — possible targets should either be the most stable isomer or at least sufficiently close in energy with a suggested upper limit of $\sim$ 125 kJ mol^{-1}.
- a weak adsorption on icy surfaces allowing the molecule to 'fly free' and therefore become detectable.

Their discussion considers aminooxirane, or 2-oxiranamine, which is chiral, and which they show lies 200 kJ mol^{-1} above acetamide, has a dipole moment of 1.0 D and an adsorption energy on water ice of 64.4 kJ mol^{-1}. Although none of these values by themselves render 2-oxiranamine undetectable it makes it unlikely, unless of course precursor species are present in high abundance. *Here* it is found that 2-oxiranamine lies 182 kJ mol^{-1} above acetamide and has a dipole moment of 1.06 D, Tables 2–3.

Complex formation between a single water molecule and 2-oxiranamine is stabilised, according to M06-2X/aug-cc-pVTZ counterpoise calculations, by $-34.3 \rightarrow -36.7$ kJ mol^{-1} depending upon the exact structure of the complex; this must be compared to values of $-36.0 \rightarrow -46.3$ kJ mol^{-1} for acetamide–water complexes — these latter agree with PBE+GD3/aug-cc-pVTZ results by Krestyaninov et al.[85] Whilst not directly comparable to the interactions between molecules and grains of water–ice in the interstellar medium it does suggest that 2-oxiranamine is somewhat more likely to 'fly freely'.

In a theoretical study[86] of the reaction between $CH_3C^{\bullet}HNH_2 + O_2$ a calculated CBS-QB3 atomisation energy of -6.1 kJ mol^{-1} is given, in conjunction with $\Delta_f H^{\circ}(0\ \mathrm{K})$ of $+37.248$ kJ mol^{-1} from ATcT[36] a formation enthalpy for 2-oxiranamine of -43.4 kJ mol^{-1} can be derived; this compares not unfavourably with the higher level result of -40.1 kJ mol^{-1} computed *here*, Table 3.

3-Methyl-oxaziridine

Postulated as a potential product in a kinetic study of the $CH_3C^{\bullet}HNH_2 + O_2$ reaction[86] while Taghizadev *et al.* investigated the structures of a number of methyl derivatives of oxaziridines.[87]

This chiral system exists mainly as *trans* with the NH and methyl group on opposite sides of the ring 71.2% with the *cis* or same side conformer at $+2.25$ kJ mol^{-1} at 28.8%.

Table 3: Results for cyclics/ kJ mol^{-1}

Species	$\Delta_f H^\circ$(0 K)	$\Delta_f H^\circ$(298.15 K)	$\langle\mu\rangle$ / D
1,2-Oxazetidine	123.7	104.6	2.852
1,3-Oxazetidine	4.1	−15.1	1.707
1-Hydroxy-aziridine	104.2	86.7	0.502
2-Aziridinol *trans*	−32.2	−50.9	1.702
2-Aziridinol *cis*	−27.5	−40.1	1.009
2-Methyl-oxaziridine	105.4	87.2	2.381
2-Oxiranamine	−40.1	−58.4	1.058
3-Methyl-oxaziridine *trans*	71.2	53.1	2.426
3-Methyl-oxaziridine *cis*	73.5	55.4	2.771

Ionisation energies

Adiabatic ionisation energies were computed with the composite method G4, IE/eV $= 27.2116 \times \{G4(0\ K)[\text{cation}] - G4(0\ K)[\text{neutral}]\}$ which has been shown to perform adequately.[88] There is good agreement with the results of the Kaiser group[13] except for the cyclics 1,3-oxazetidine and 3-methyl-oxaziridine which have been mis-tabulated[89] as 9.43 and 9.02 eV, respectively, instead of 9.02 and 9.43 eV, see Table 4, and for methylene-amino-methanol which can be rationalised because *here* the lowest energy conformer with $\angle$ CNCO $= 0^\circ$ is considered as opposed to what is probably a *gauche* conformer.

There are very few experimental measurements against which these results can be compared. The electron/ion coincidence spectroscopic data of Schwell et al. yielded 9.71 eV for acetamide[48] as against a computed 9.70 eV but for N-methyl formamide the calculated value of 9.79 eV is wildly at odds with the 9.55 eV obtained in a photoionisation mass spectrometric study by Leach and co-workers.[62]

In addition atomisation energies and consequently formation enthalpies at 0 K were tabulated, Table 4, and compared to the higher level results in Tables 2–3 by means of a Bland–Altman[90] plot, Fig. 13. The bias, that is the average deviation of G4 from the higher level methods is a modest 0.39 kJ mol^{-1}. The most obvious deviations are shown by the nitrenes in their triplet state, Fig. 13, which is not totally unexpected.

Table 4: G4 Results

Species	$\Delta_f H^\ominus$(0 K)	IE / eV	
Name	kJ mol^{-1}	Calc.	Lit.[13]
1-Amino-ethenol	−117.4	7.86	7.88
2-Amino-ethenol *Z*	−91.2	7.42	7.39
2-Amino-ethenol *E*	−82.6	7.61	
2-Imino-ethanol *E*	−84.0	9.53	9.51
2-Imino-ethanol *Z*	−96.0	9.74	
Acetamide	−218.3	9.70	9.74
Amino-acetaldehyde	−114.0	9.12	9.12
Ethanimidic acid *E,Z*	−171.5	9.72	9.65
Methylene-amino-methanol	−69.7	9.39	9.18
Methyl formimidate (*E*, ap)	−105.3	9.80	
Methyl formimidate (*Z*, sp)	−89.3	9.69	9.71
N-hydroxy-ethenamine	58.7	8.14	
Nitroso-ethane	58.5	8.91	
N-methyl-formamide *cis*	−171.6	9.79	9.80
N-methyl-methanimidic acid	−124.3	9.44	
N-methyl-nitrone	60.4	9.02	9.02
C-methyl-nitrone *Z*	37.6	8.88	
C-methyl-nitrone *E*	49.6	8.16	
O-ethenyl-hydroxylamine	82.0	8.83	8.79
O-methyl-oxime-formadehyde *E*	49.4	9.49	9.51
Oxime-acetaldehyde *cEt*	−5.5	9.76	
Oxime-acetaldehyde *tZt*	−3.2	9.55	
Carbenes & Nitrenes			
Amino-hydroxymethyl-carbene ^{1}A$'$	39.2	7.89	
Hydroxy-methylamino-carbene ^{1}A$'$	−19.1	8.09	
Methoxy-amino-carbene ^{1}A$'$	3.0	8.01	
2-Hydroxy-ethyl-imidogen ^{3}A	159.2	7.11	
Ethoxy-imidogen ^{3}A$''$	204.1	8.16	
Methoxy-methyl-imidogen ^{3}A$''$	206.6	9.85	
Cyclics			
1,2-Oxazetidine	124.7	8.21	
1,3-Oxazetidine	4.0	9.00	9.43
1-Hydroxy-aziridine	103.6	9.00	
2-Aziridinol *trans*	−31.6		
2-Aziridinol *cis*	−27.0		
2-Methyl-oxaziridine	103.5	9.11	
2-Oxiranamine	−40.0		
3-Methyl-oxaziridine *trans*	70.9	9.45	
3-Methyl-oxaziridine *cis*	73.5	9.41	9.02

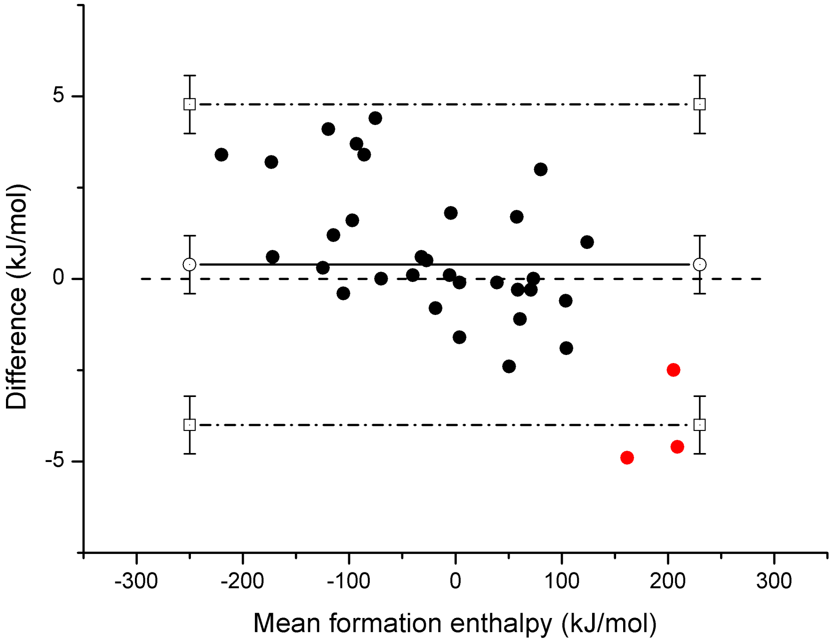


Figure 13: High-level and G4 $\Delta_f H^\circ$(0 K): bias —, limits of agreement –·–·; nitrenes ●

Likely candidates

If the criteria outlined by Ellinger et al. are decisive in determing whether a particular species is detectable or not then it is unlikely that any of the chiral cyclic molecules featured here will qualify.[84]

More generally are any of the acyclics likely candidates? If only those species which lie within an arbitrary 100 kJ mol^{-1} are worthy of consideration then 1-amino ethenol, amino acetaldehyde, ethanimidic acid, methyl formimidate and N-methyl methanimidic acid qualify. However all of these have dipole moments towards the lower end of the scale. Another consideration that can impact on the detectability of these compounds are the number of low-lying conformers which effectively reduces the population and hence the intensity of a particular rotational transition.

In the absence of comprehensive chemical kinetic mechanisms for the formation of species in the interstellar medium, including the key compound acetamide, it is difficult to propose routes to the candidate C_2H_5NO molecules. Given that acetamide is present in high abundance it is not unreasonable to look at this as a possible source and then it can be noted that simple H-atom transfer reactions, Fig. 18, link acetamide to 1-amino ethenol and to (*E,Z*) ethanimidic acid, Fig. 3, whilst the reasonably abundant (*Z*) rotamer of N-methyl formamide is linked to (*E,Z*) N-methyl formimidic acid, Fig. 8.

Some have explored the opposite approach, that is the formation of higher-energy isomers from which lower energy species would emerge;[37,92] so for example Foo et al. have considered bimolecular (not of interest *here*) and unimolecular routes to acetamide — the latter from N-methyl formamide, acetimidic (ethanimidic) acid, 1-amino ethenol and 2-amino acetaldehyde.[15] They show that the energy barrier for (*E,Z*) acetimidic acid → acetamide is 119 kJ mol^{-1} (*this work* 130 kJ mol^{-1}) whilst the barrier for *anti* 1-amino ethenol → acetamide is 170 kJ mol^{-1}; the latter agrees well with values of 164 and 168 kJ mol^{-1} from Mardyukov[37] and *this work*, respectively.

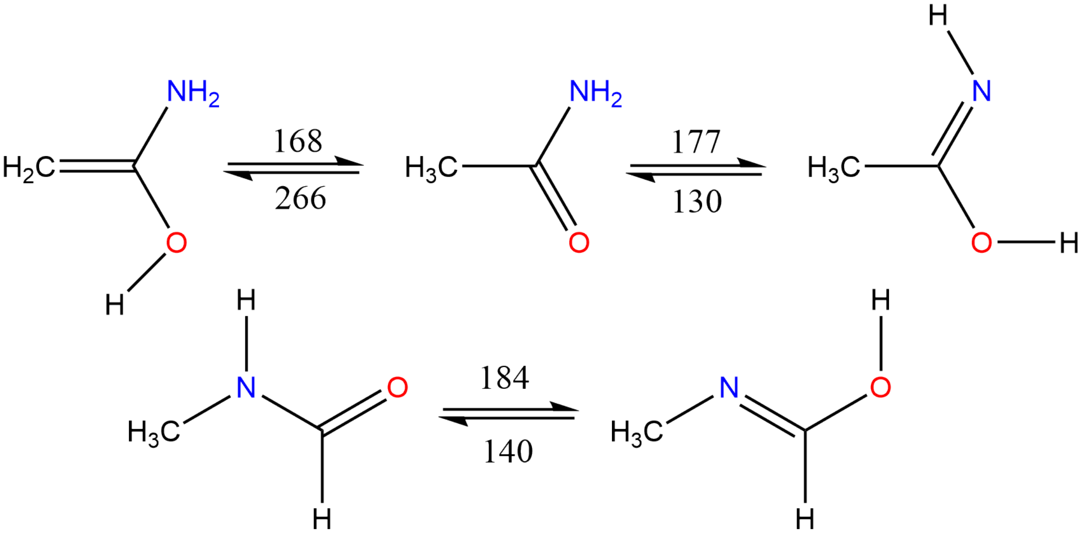


Figure 14: H-transfer reactions; forward and reverse barriers / kJ mol^{-1}

Whilst it is true that a barrier of 168 kJ mol^{-1} renders the process, $H_2C{=}C(OH)NH_2 \longrightarrow H_3C{-}C(O)NH_2$, unfeasible thermally, tunnelling plays an increasing role at temperatures less than 300 K. So for the 1,3[H]-transfer reaction from (*E,Z*) ethanimidic acid to acetamide an approximate rate constant of $k \approx 1.6 \times 10^{-11}$ s^{-1} at 100 K can be calculated, by the

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Given that species with the C≡N bond are abundant (27 such have been detected[94]) one might speculate that acid-induced addition of H_2O could provide a feasible channel:

$$\mathrm{CH_3{-}C{\equiv}N} \xrightarrow{\mathrm{H_3O^+}} \mathrm{CH_3{-}C{\equiv}N^+H} \longrightarrow \mathrm{CH_3{-}C(O^+H_2){=}NH} \xrightarrow{\mathrm{H_2O}} \mathrm{CH_3{-}C(OH){=}NH + H_3O^+}$$

presumably on water–ice grains. It is known experimentally that H_3O^+ exists as protonic defects in the lattice as a result of UV photolysis of ice and as stated by Moon et al. "H_3O^+ may have a substantial population in interstellar ice in UV-irradiating environments and participate in acid-base reactions in the solid phase" as well as being detected in the ISM.[95,96]

The reaction between H−C≡N and H_2O to form firstly methanimidic acid, HC(OH)=NH, and then formamide, HC(O)−NH_2, has been shown not to be competitive, despite the co-operation of additional water molecules, due to a high energy barrier by Rimola et al. in theoretical calculations of this reaction on a 33-H_2O ice cluster model.[97] A view reinforced by Darla et al. in ωB97xD/aug-ccpVTZ gas-phase calculations in which they show that neither the presence of an additional water molecule as a participant or as a spectator makes a sufficient reduction in the barriers to reaction to render the process kinetically significant.[98]

Woon has shown in density functional calculations of a cluster of 24 water molecules that $C^+(^2P)$ reacts with H−C≡N to form a transient species H−C=N−C^+ firstly, which then reacts with a neighbouring H_2O to form H−C(OH_2)=N−C^+ which then loses a proton from the O-atom to a water molecule forming, H−C(OH)=NC + H_3O^+ — "the entire process has no activation barriers whatsoever".[99]

Under severe conditions[100] the methanimidic acid can be further protonated at the N-atom, $CH_3C(OH){=}N^+H_2 \longleftrightarrow CH_3C(O^+H){-}NH_2$, and then deprotonated at O to yield the amide directly, $CH_3C(O)NH_2$, and indeed even further to a carboxylic acid, $CH_3C(O)OH$, but it is unclear whether such severe conditions would apply in the ISM.

Direct confirmation of this speculation, that is the acid-induced water addition to methyl cyanide, might be difficult to obtain since ethanimidic acid is probably less easily detectable due to its much lower dipole moment in comparison to acetamide, although the not unrelated ethanimime, $CH_3{-}CH{=}NH$, has been found in a survey of Sagittarius B2 North in both (Z) and (E) conformations.[101] Note that a counterpoise M06-2X/aug-cc-pVTZ calculation shows that (E,Z)-ethanimidic acid is somewhat more strongly bound (-52.8 kJ mol^{-1}) than acetamide ($-36.0 \rightarrow -46.3$ kJ mol^{-1}) by a single water molecule — an indication that it might be less likely to fly freely.

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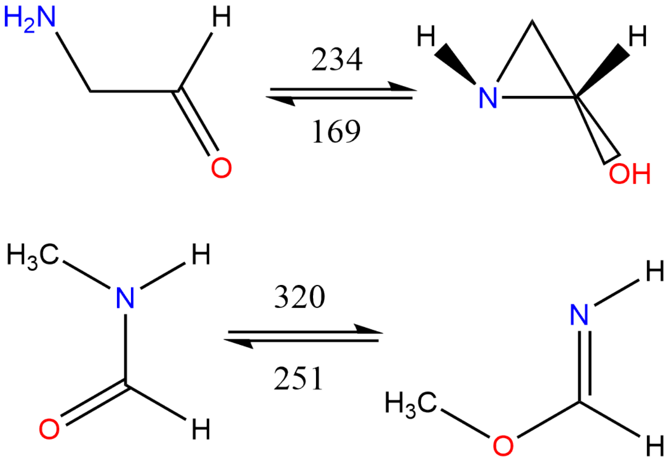

Figure 15: Speculative reactions; forward and reverse barriers / kJ mol^{-1}

High energy species

Additional calculations were carried out for a number of mainly dipolar species derived from the Foo et al. work;[15] these are shown in Fig. 17 and cross-referenced to Table 5. These molecules are characterised by large dipole moments, unsurprisingly, with species (g) outstanding at $\langle\mu\rangle = 9.14$ D. Of the five cyclic compounds present none of them appear to be likely candidates for detection since they do not fit the Ellinger criteria.[84] Although there has been a tentative detection of aziridine[91] in hot cores around young stars, the aziridine N-oxide, Fig. 17q, does have an enhanced dipole moment vis-à-vis aziridine which would make it more liable for detection since it yet retains the high symmetry and rigid structure of its parent. However, apart probably from the nitrone, Fig. 17f, which corresponds to *Z* C-methyl nitrone discussed earlier and whose values are listed in Table 2, *energetically* these compounds are unlikely to be of relevance based on our current understanding of conditions in the ISM.

An indication of the complexity of this system can be gained from the fact that an attempt to carry out a ring closure reaction from acetamide, in the expectation that 3-methyl oxaziridine would be formed, proved illusory, Fig. 16. Yet another dipolar compound is formed whose formation enthalpy of 312.4 kJ mol^{-1} (296.1 at 298.15 K) and dipole moment of 3.88 D makes it akin to species (c) of Fig. 17. A similar attempt to ring-close N-methyl formamide resulted in structure (u), Fig. 17, for which $\Delta_f H^\circ(0\text{ K}) = 330.0$ kJ mol^{-1} (313.5 at 298.15 K) and $\langle\mu\rangle = 4.89$ D — clearly this system exhibits quite a diversity of chemical bonding.

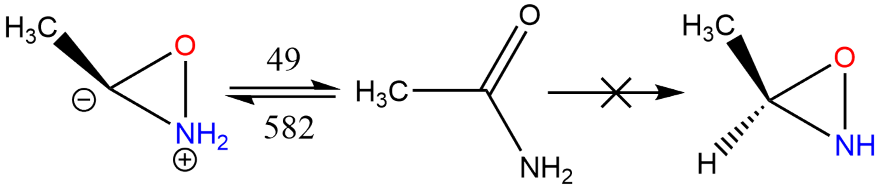

Figure 16: Ring closure / kJ mol^{-1}

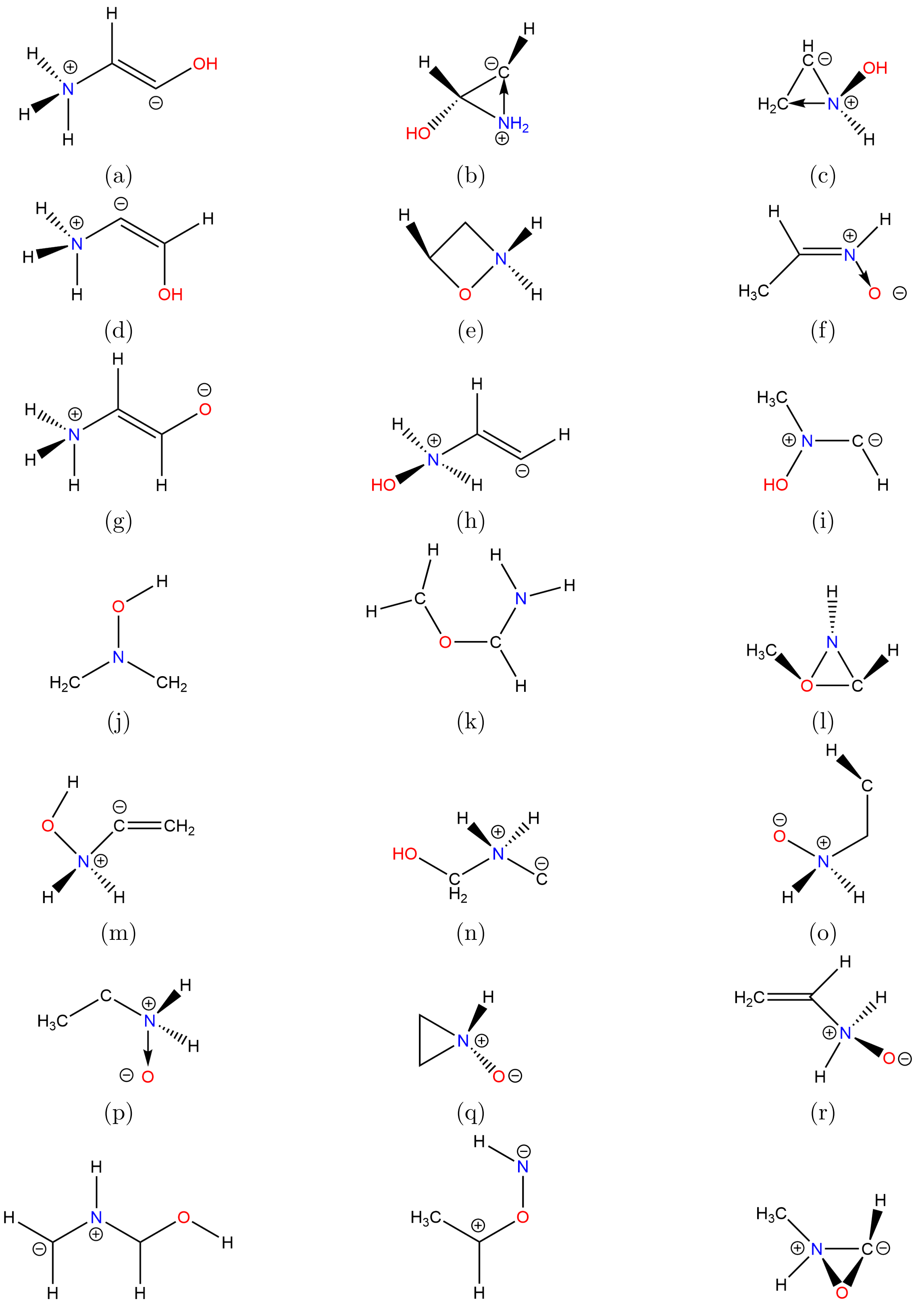
(a) (b) (c)
(d) (e) (f)
(g) (h) (i)
(j) (k) (l)
(m) (n) (o)
(p) (q) (r)
(s) (t) (u)

Figure 17: Structures of dipolar species

Table 5: Dipolar species: kJ mol^{-1}

Fig. 17	$\Delta_f H^{\ominus}(0\ K)$	$\Delta_f H^{\ominus}(298.15\ K)$	$\langle\mu\rangle$ / D
(a)	185.2	169.6	6.46
(b)	177.0	160.8	5.22
(c)	310.8	293.6	2.49
(d)	153.4	138.4	4.31
(e)	421.5	403.9	6.41
(f)	37.6	22.0	3.50
(g)	65.5	50.1	9.14
(h)	328.0	312.6	3.67
(i)	182.3	167.1	1.36
(j)	197.6	181.6	0.81
(k)	141.6	126.7	3.60
(l)	415.4	399.9	3.14
(m)	287.0	272.6	3.29
(n)	522.2	507.6	5.36
(o)	475.8	460.3	4.67
(p)	412.1	397.6	1.83
(q)	195.7	178.0	4.86
(r)	222.3	206.9	4.87
(s)	169.7	153.5	4.78
(t)	80.6	66.2	1.45
(u)	330.0	313.5	4.89

Likely candidates

If the criteria outlined by Ellinger et al. are decisive in determing whether a particular species is detectable or not then it is unlikely that any of the chiral cyclic molecules featured here will qualify.[84]

More generally are any of the acyclics likely candidates? If only those species which lie within an arbitrary 100 kJ mol^{-1} are worthy of consideration then 1-amino ethenol, amino acetaldehyde, ethanimidic acid, methyl formimidate and N-methyl methanimidic acid qualify. However all of these have dipole moments towards the lower end of the scale. Another consideration that can impact on the detectability of these compounds are the number of low-lying conformers which effectively reduces the population and hence the intensity of a particular rotational transition.

In the absence of comprehensive chemical kinetic mechanisms for the formation of species in the interstellar medium, including the key compound acetamide, it is difficult to propose routes to the candidate C_2H_5NO molecules. Given that acetamide is present in high abundance it is not unreasonable to look at this as a possible source and then it can be noted that simple H-atom transfer reactions, Fig. 18, link acetamide to 1-amino ethenol and to (*E,Z*) ethanimidic acid, Fig. 3, whilst the reasonably abundant (*Z*) rotamer of N-methyl formamide is linked to (*E,Z*) N-methyl formimidic acid, Fig. 8.

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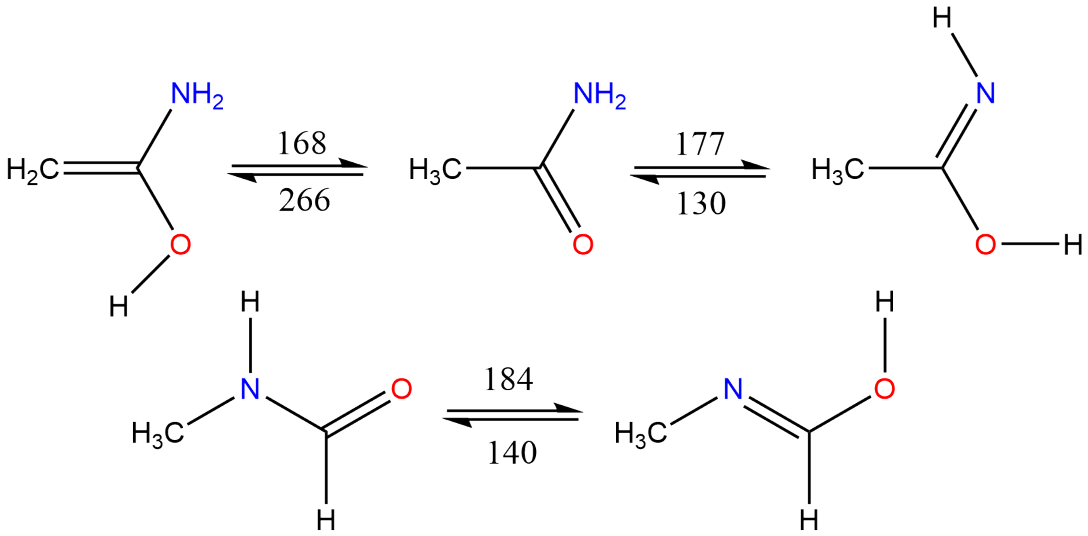

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Given that species with the C≡N bond are abundant (27 such have been detected[94]) one might speculate that acid-induced addition of H_2O could provide a feasible channel:

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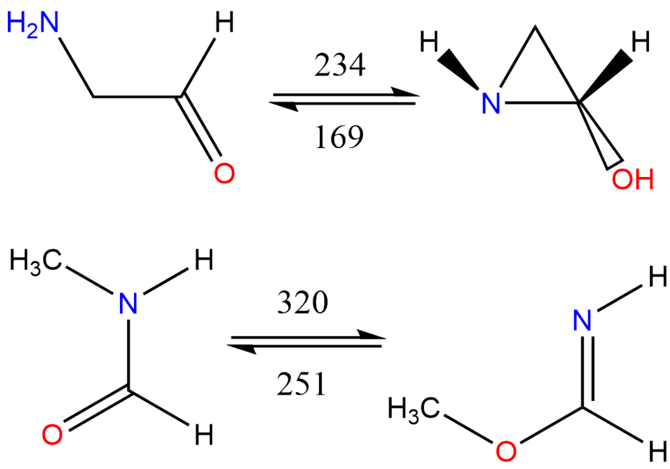

Figure 19: Speculative reactions; forward and reverse barriers / kJ mol^{-1}

Conclusions

High-level ab initio atomisation energy calculations have been carried out to rank a number of ‘known’ C_2H_5NO neutral molecules from the most stable, acetamide, to the least, methoxy methyl imidogen. Additionally dipole moments and adiabatic ionisation energies are reported and compared to the literature — what little of it exists. Higher energy species incorporating more diverse types of bonding than the traditional tetravalent carbon, trivalent nitrogen and divalent oxygen are also documented.

An alternative scheme is outlined to explain acetamide formation routes in the ISM; kinetically, tunnelling in a 1,3[H]-transfer reaction from a higher-energy isomer, ethanimidic acid, seems to offer a possible channel which is probably more reasonable than the current examples[2,3,102] in the literature:

$$NH_2CHO + CH_2 \longrightarrow CH_3CONH_2 + h\nu$$

$$\mathrm{NH_2CHO + CH_3{}^+ \longrightarrow CH_3CHONH_2{}^+ + h\nu}$$
$$\mathrm{CH_3CHONH_2{}^+ + e^- \longrightarrow CH_3CONH_2 + H^\bullet}$$
$$\mathrm{NH_2CHO + CH_5{}^+ \longrightarrow CH_3CHONH_3{}^+ + H_2}$$
$$\mathrm{CH_3CHONH_3{}^+ + e^- \longrightarrow CH_3CONH_2 + H^\bullet}$$
$$\mathrm{CH_3{}^\bullet + NH_2CO^\bullet \longrightarrow CH_3CONH_2}$$

A general mechanism is then needed to generate this imidic acid from more abundant precursors and it is proposed that an acid-induced water addition to carbon-nitrogen triple bonds, hosted on water-ice grains, not the gas-phase, of $\mathrm{R{-}C{\equiv}N \xrightarrow[H_3O^+]{H_2O} RC(OH){=}NH}$, meets this requirement. The auto-catalytic nature of this reaction is a point in its favour as well as the fact that the more direct addition $\mathrm{R{-}C{\equiv}N \xrightarrow{H_2O} RC(OH){=}NH}$ has been discounted.[97,98]

Since this system exhibits quite a range of bonding, even within the restrictive context of neutral and closed-shell molecules, the results are likely to be useful for incorporation into databases for artificial intelligence learning/predictive efforts — ameliorating the well-known problem of dataset bias.

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Supporting Information

The document contains the Cartesian coordinates, rotational constants, frequencies and energetics of species discussed in the main text.

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The Irish Centre for High-End Computing, ICHEC, is thanked for the provision of computational resources (projects: nuig02, ngche100c) as are professors Hans-Joachim Werner (Stuttgart) and Peter J. Knowles (Cardiff) for the granting of a personal Molpro license. M. A. Krestyaninov (G. A. Krestov Institute of Solution Chemistry of the RAS) kindly provided initial structures of various acetamide–water complexes as did Béla Fiser (Miskolc) who generously furnished the set of 53 Cartesians of acetamide isomers. Niels Ligterink (Bern) for interesting discussions.

Declaration

The author declares no competing financial interest.

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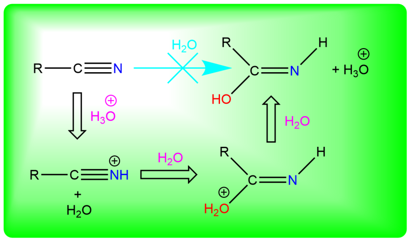
Appendix

Table 6: Rotational and centrifugal distortion constants for ethanimidic acid: B3LYP/cc-pVTZ

Parameter	A	Parameter	S	Units
Δ_J	8.2251	D_J	9.3647	/ kHz
Δ_K	-0.6276	D_{JK}	-13.6660	/ kHz
Δ_{JK}	-6.8283	D_K	5.0705	/ kHz
δ_J	0.4028	d_1	-0.4028	/ kHz
δ_K	14.4050	d_2	0.5698	/ kHz
Φ_J	0.0102	H_J	0.01699	/ Hz
Φ_K	-0.5807	H_K	-0.01039	/ Hz
Φ_{JK}	0.2382	H_{JK}	-0.05579	/ Hz
Φ_{KJ}	-0.8291	H_{KJ}	0.04914	/ Hz
ϕ_J	0.000378	h_1	0.00288	/ Hz
ϕ_K	-1.3726	h_2	-0.00339	/ Hz
ϕ_{JK}	0.1291	h_3	-0.00251	/ Hz
$A_0 = 10799.95, B_0 = 9258.12, C_0 = 5138.04$ / GHz				


R—C≡N
H_2O
R, C=N, H, HO
+ $H_3O^{\oplus}$
$H_3O^{\oplus}$
H_2O
R—C≡$NH^{\oplus}$
+
H_2O
H_2O
R, C=N, H, $H_2O^{\oplus}$