Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Structures, Proton Transfer and Dissociation of Hydroxylammonium Nitrate (HAN) Revealed by Tandem Electrospray Ionization Mass Spectrometry and Molecular Dynamics Simulations

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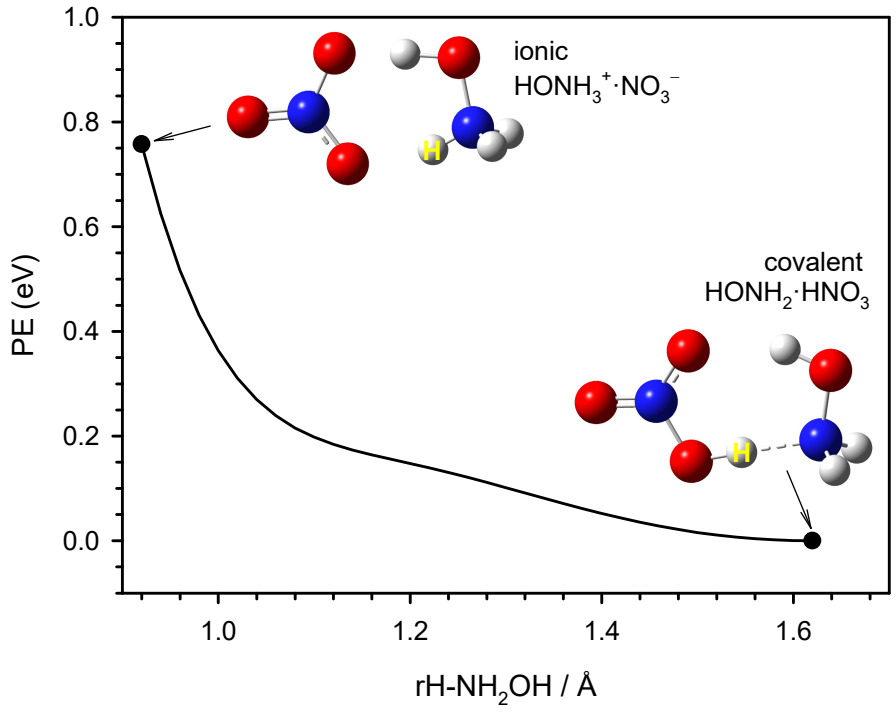

Fig. S1 A relaxed PES scan along the proton transfer coordinate within $HONH_2 \cdot HNO_3$, calculated at the ωB97XD/6-31+G(d,p) level of theory.

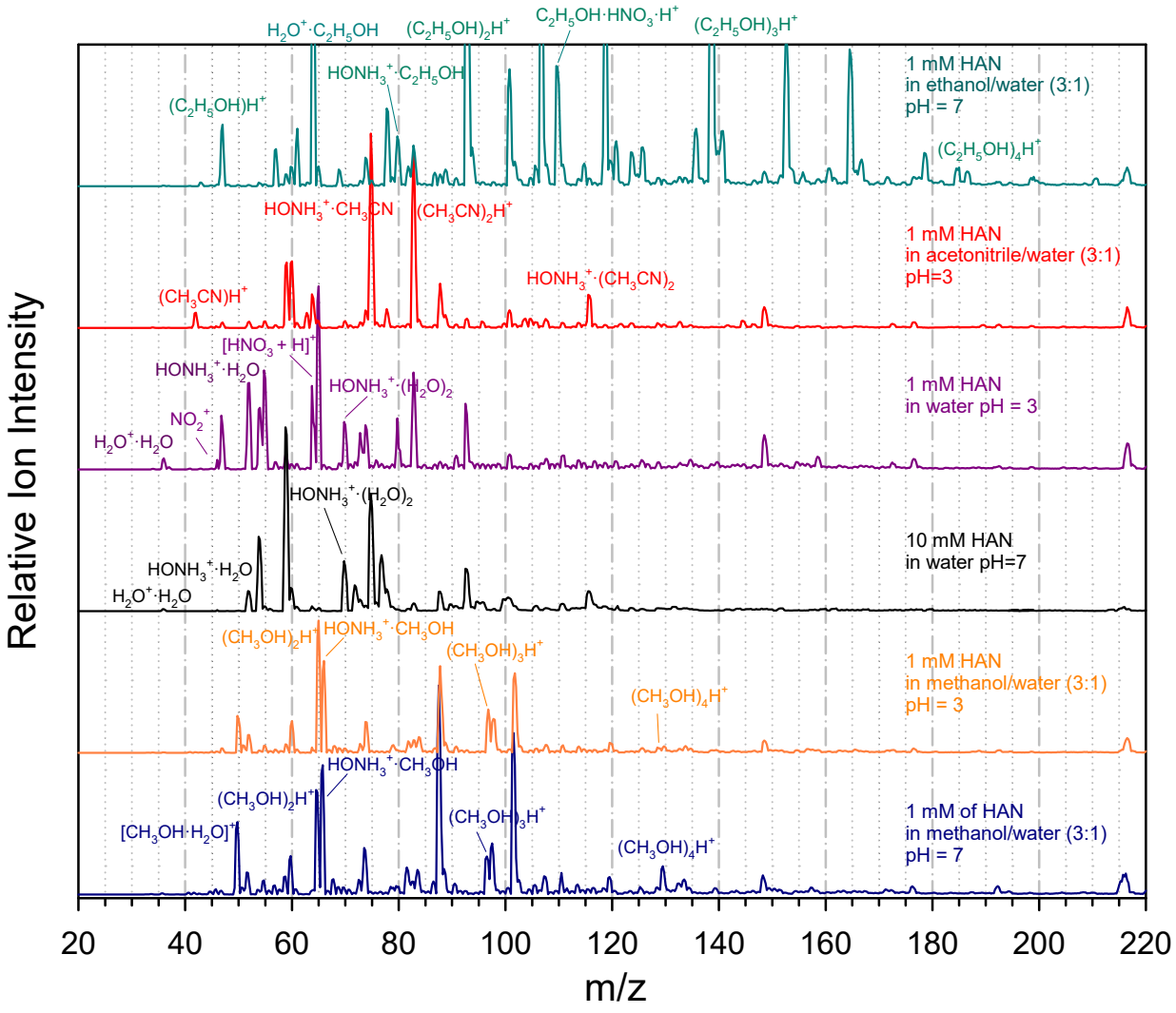

Fig. S2 Positive ESI mass spectra of HAN measured in various solvents and at pH = 3 and 7, respectively. Note that the ESI ion intensity of a typical 1 mM cation solution is ~ 1 $\times 10^6$ counts/s measured at an ESI voltage of ~ +2.3 kV. However, a much higher voltage (+3.4 kV) was required to initiate electrospray of HAN solutions, and the maximum ion intensity in these mass spectra was only < 5 $\times 10^4$ counts/s. The lack of any obvious intact HAN species in the positive ESI mass spectra indicates the use of HAN in electrospray could result in a significant loss of thrust because of neutralization and/or the presence of other reactive channels.

Cartesian coordinates optimized at ωB97XD/6-31+G(d,p)

$HONH_2 \cdot HNO_3$

N1 1.971556 0.649636 -0.000106
H2 2.447331 1.025105 -0.818687
H3 2.446977 1.025483 0.818508
O4 2.247171 -0.737888 0.000278
H5 1.361950 -1.138561 0.000124
N6 -1.272523 -0.071090 -0.000036
O7 -0.639365 1.114339 -0.000028
H8 0.374782 0.922287 -0.000344
O9 -0.575833 -1.083584 -0.000316
O10 -2.472508 -0.028384 0.000241

Rotational constants (GHz): 8.5838351 1.7886277 1.4920015

Zero-point correction= 0.071173 (Hartree/Particle)
Thermal correction to Energy= 0.078119
Thermal correction to Enthalpy= 0.079063
Thermal correction to Gibbs Free Energy= 0.039155
Sum of electronic and zero-point Energies= -412.451598
Sum of electronic and thermal Energies= -412.444652
Sum of electronic and thermal Enthalpies= -412.443708
Sum of electronic and thermal Free Energies= -412.483616

$^{-}O_3N \cdot HONH_3^{+} \cdot NO_3^{-}$

N1 -0.141098 0.494491 0.059375
H2 -1.015402 0.424225 -0.539795
H3 -0.503652 0.415107 1.013587
O4 0.499712 1.721651 -0.137889
H5 1.460406 1.499297 0.029094
N6 3.087451 -0.381106 -0.012106
O7 2.081226 -1.045059 -0.393567
H8 0.551579 -0.267003 -0.136393
O9 2.921703 0.820928 0.361972
O10 4.205098 -0.886003 0.002579
N11 -3.202048 -0.255415 0.028178
O12 -2.565230 0.131948 -1.007037
O13 -2.575340 -0.376128 1.111297
O14 -4.405052 -0.502015 -0.049182

Rotational constants (GHZ): 3.4585888 0.3777837 0.3611731

Zero-point correction= 0.088034 (Hartree/Particle)
Thermal correction to Energy= 0.099337
Thermal correction to Enthalpy= 0.100281
Thermal correction to Gibbs Free Energy= 0.046866

Sum of electronic and zero-point Energies= -692.780781
Sum of electronic and thermal Energies= -692.769478
Sum of electronic and thermal Enthalpies= -692.768534
Sum of electronic and thermal Free Energies= -692.821949

***cyclic*-[$HONH_3^+ \cdot NO_3^- \cdot HONH_3^+ \cdot NO_3^-$]**

N1 -1.577896 -1.452901 0.852240
H2 -1.085875 -1.971192 0.090218
H3 -1.544945 -1.995275 1.713878
O4 -2.922254 -1.217484 0.550470
H5 -2.901822 -0.331744 0.109395
N6 -1.218835 1.625093 -0.263104
O7 -0.598193 1.064182 0.723973
H8 -1.081956 -0.532999 0.980311
O9 -2.331834 1.181474 -0.590473
O10 -0.674674 2.558982 -0.838135
N11 2.027697 1.405155 0.240596
H12 2.441985 2.329324 0.139221
H13 1.001318 1.469463 0.484815
O14 2.724820 0.748710 1.259976
H15 2.344913 -0.166661 1.202188
N16 1.119512 -1.469727 -0.618366
O17 1.892981 -0.826164 -1.350705
H18 2.117954 0.843468 -0.631025
O19 1.208453 -1.361810 0.645413
O20 0.232587 -2.197605 -1.096589

Rotational constants (GHz): 0.8878585 0.6893278 0.4883460

Zero-point correction= 0.146906 (Hartree/Particle)
Thermal correction to Energy= 0.161463
Thermal correction to Enthalpy= 0.162407
Thermal correction to Gibbs Free Energy= 0.103813
Sum of electronic and zero-point Energies= -824.931707
Sum of electronic and thermal Energies= -824.917151
Sum of electronic and thermal Enthalpies= -824.916207
Sum of electronic and thermal Free Energies= -824.974800