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Enthalpies of Formation of Gas-Phase N_3 , N_3^- , N_5^+ , and N_5^- from Ab Initio Molecular Orbital Theory, Stability Predictions for $N_5^+N_3^-$ and $N_5^+N_5^-$, and Experimental Evidence for the Instability of $N_5^+N_3^-$

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Enthalpies of Formation of Gas-Phase N₃, N₃⁻, N₅⁺, and N₅⁻ from Ab Initio Molecular Orbital Theory, Stability Predictions for N₅⁺N₃⁻ and N₅⁺N₅⁻, and Experimental Evidence for the Instability of N₅⁺N₃⁻

Abstract

Ab initio molecular orbital theory has been used to calculate accurate enthalpies of formation and adiabatic electron affinities or ionization potentials for N₃, N₃⁻, N₅⁺, and N₅⁻ from total atomization energies. The calculated heats of formation of the gas-phase molecules/ions at 0 K are $\Delta H_f(N_3(2\Pi)) = 109.2$, $\Delta H_f(N_3-(1\Sigma^+)) = 47.4$, $\Delta H_f(N_5-(1A_1')) = 62.3$, and $\Delta H_f(N_5+(1A_1)) = 353.3$ kcal/mol with an estimated error bar of ± 1 kcal/mol. For comparison purposes, the error in the calculated bond energy for N₂ is 0.72 kcal/mol. Born–Haber cycle calculations, using estimated lattice energies and the adiabatic ionization potentials of the anions and electron affinities of the cations, enable reliable stability predictions for the hypothetical N₅⁺N₃⁻ and N₅⁺N₅⁻ salts. The calculations show that neither salt can be stabilized and that both should decompose spontaneously into N₃ radicals and N₂. This conclusion was experimentally confirmed for the N₅⁺N₃⁻ salt by low-temperature metathetical reactions between N₅SbF₆ and alkali metal azides in different solvents, resulting in violent reactions with spontaneous nitrogen evolution. It is emphasized that one needs to use adiabatic ionization potentials and electron affinities instead of vertical potentials and affinities for salt stability predictions when the formed radicals are not vibrationally stable. This is the case for the N₅ radicals where the energy difference between vertical and adiabatic potentials amounts to about 100 kcal/mol per N₅.

Disciplines

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Comments

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Abstract: Ab initio molecular orbital theory has been used to calculate accurate enthalpies of formation and adiabatic electron affinities or ionization potentials for N_3 , N_3^- , N_5^+ , and N_5^- from total atomization energies. The calculated heats of formation of the gas-phase molecules/ions at 0 K are $\Delta H_f(N_3(^2\Pi)) = 109.2$, $\Delta H_f(N_3^-(^1\Sigma^+)) = 47.4$, $\Delta H_f(N_5(^1A_1)) = 62.3$, and $\Delta H_f(N_5^+(^1A_1)) = 353.3$ kcal/mol with an estimated error bar of ± 1 kcal/mol. For comparison purposes, the error in the calculated bond energy for N_2 is 0.72 kcal/mol. Born–Haber cycle calculations, using estimated lattice energies and the adiabatic ionization potentials of the anions and electron affinities of the cations, enable reliable stability predictions for the hypothetical $N_5^+N_3^-$ and $N_5^+N_5^-$ salts. The calculations show that neither salt can be stabilized and that both should decompose spontaneously into N_3 radicals and N_2 . This conclusion was experimentally confirmed for the $N_5^+N_3^-$ salt by low-temperature metathetical reactions between N_5SbF_6 and alkali metal azides in different solvents, resulting in violent reactions with spontaneous nitrogen evolution. It is emphasized that one needs to use adiabatic ionization potentials and electron affinities instead of vertical potentials and affinities for salt stability predictions when the formed radicals are not vibrationally stable. This is the case for the N_5 radicals where the energy difference between vertical and adiabatic potentials amounts to about 100 kcal/mol per N_5 .

Introduction

The discovery of stable N_5^+ salts,^{1,2} the long-known existence of stable N_3^- salts,³ and the recent experimental detection of the N_5^- anion⁴ have stimulated research in polynitrogen chemistry and a search for nitrogen allotropes. The high endothermicity of polynitrogen compounds renders their preparation and handling very difficult, and reliable stability predictions are important for the selection of suitable target compounds. The enthalpies of formation of crucial species, such as N_3 , N_3^- , N_5 , N_5^+ , and N_5^- , are not accurately known from experiment, because of the difficulty in handling these com-

pounds and ions. There have been a number of theoretical studies on allotropes of nitrogen using ab initio molecular orbital theory without the use of empirical parameters, but these studies have not reliably established the energetics of these compounds. In particular, we note the extensive work of the Bartlett group on these species,^{5,6} the work of Nguyen and Ha on decomposition mechanisms for N_5^x , $x = -1, 0, +1$,⁷ and that of Martin and co-workers on N_3 .⁸ Several theoretical studies on the stability of $N_5^+N_3^-$ and $N_5^+N_5^-$ have been published.^{5,6,9} In the most recent work, Fau, Wilson, and Bartlett performed ab initio MP2 and CCSD(T) molecular orbital theory and B3LYP density functional theory calculations on $N_5^+N_5^-$ and $N_5^+N_3^-$ and their individual ions as well as on quasi-periodic clusters of $N_5^+N_5^-$. This work suggested that on a closed shell singlet surface the $N_5^+N_5^-$ ion pair is stable to dissociation into the

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- (1) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004.
- (2) Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308.
- (3) Curtius, T. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 3023.
- (4) Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Christe, K. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3051.

(5) Fau, S.; Bartlett, R. J. *J. Phys. Chem. A* **2001**, *105*, 4096.

(6) Fau, S.; Wilson, K. J.; Bartlett, R. J. *J. Phys. Chem. A* **2002**, *106*, 4639.

(7) Nguyen, M. T.; Ha, T.-K. *Chem. Phys. Lett.* **2001**, *335*, 311. Nguyen, M. T.; Ha, T.-K. *Chem. Phys. Lett.* **2000**, *317*, 135.

(8) Martin, J. M. L.; Francois, J. P.; Gijbels, R. *J. Chem. Phys.* **1990**, *93*, 4485.

(9) Gagliardi, L.; Orlandi, G.; Evangelisti, S.; Roos, B. O. *J. Chem. Phys.* **2001**, *114*, 10733.

cation and anion by 114 kcal/mol but is still ~ 300 kcal/mol above $5N_2$ molecules. Thus, the singlet coupled ion pair represents a metastable structure on the potential energy surface. Approximate transition state searches suggested that the singlet coupled ion pair is stable by 15–25 kcal/mol to dissociation for the channel producing N_3 and N_2 . These authors also suggested that $N_5^+N_3^-$ is unlikely to be stable. The authors noted that this is consistent with their calculated vertical electron affinity and ionization potential calculations, suggesting that the $N_5^+N_3^-$ ion pair is less ionic than the $N_5^+N_5^-$ ion pair because the high ionization potential of N_5^- , relative to that of N_3^- , causes in $N_5^+N_5^-$ effective resistance to charge transfer from the anion to the cation.⁶

This interesting concept and our own interests in such compounds led us to perform a different set of calculations on the stability of these compounds. We have also used high level ab initio molecular orbital theory to address the important question of whether the combination of a stable polynitrogen cation, such as N_5^+ , with a stable polynitrogen anion, such as N_3^- , can lead to a stable ionic nitrogen allotrope, such as $N_5^+N_3^-$. The stability predictions were made using Born–Haber cycles, a well-established and widely used method¹⁰ for evaluating the stability of ionic salts, if reliable values for the lattice energies of the salts, the first ionization potential of the anion, and the electron affinity of the cation are available. This approach also requires an excellent knowledge of the nature and stability of the most likely decomposition products.

A critical prerequisite for such stability calculations is the use of accurate heats of formation and electron affinities and ionization potentials. We have developed an approach¹¹ to the reliable calculation of molecular thermodynamic properties, notably enthalpies of formation, based on ab initio molecular orbital theory without using empirical parameters. Our approach involves an accurate calculation of the total atomization energy of a molecule and combines this value with known enthalpies of formation of the atoms to calculate the molecular enthalpy of formation at 0 K. This method starts with coupled cluster theory, including a perturbative triples correction (CCSD(T)),^{12–14} combined with the correlation-consistent basis sets^{15,16} extrapolated to the complete basis set (CBS) limit to treat the correlation energy of the valence electrons. This step is followed by a number of smaller corrections that are presumed to be additive, including core–valence interactions and relativistic effects, both scalar and spin–orbit. Finally, one must include the zero-point energy obtained from experiment, theory, or some combination.

The standard enthalpies of formation of compounds at 298 K can then be calculated from the 0 K value and other calculated properties by using standard thermodynamic and statistical mechanics expressions.¹⁷

This paper provides a conclusive answer to the question of whether the lattice energies of these salts are sufficient to stabilize them as solids, thus preventing spontaneous electron transfer from the anion to the cation and spontaneous decomposition. Furthermore, for $N_5^+N_3^-$, experimental data are provided in support of our theoretical predictions.

Experimental Section

Caution! Reactions of N_5^+ salts with azide ions are violent and can result in explosions. Therefore, these materials should be handled only on a small scale with appropriate safety precautions (face shield, leather gloves, and protective clothing).

Materials and Apparatus. All reactions were carried out in a Teflon-PFA double U-tube apparatus that consisted of a reaction U-tube, a porous Teflon filter assembly, and a receiver U-tube. Volatile materials were handled on a stainless steel/Teflon-FEP vacuum line.¹⁸ Nonvolatile solids were handled in the dry nitrogen atmosphere of a glovebox. Infrared spectra were recorded on a Mattson Galaxy FT-IR spectrometer using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd:YAG laser at 1064 nm and Pyrex melting point capillaries as sample containers.

The N_5SbF_6 was prepared using our previously reported procedure.² The CsN_3 (Aldrich Chemical Co.) was pretreated with an excess of $(CH_3)_3SiN_3$ to remove any traces of moisture. The SO_2 (Air Products) was used as received.

Reactions of N_5SbF_6 with CsN_3 . In a typical experiment, N_5SbF_6 (2.285 mmol) and CsN_3 (2.267 mmol) were loaded in the drybox into a Teflon-PFA reaction vessel that was closed by a Teflon valve. On the vacuum line, anhydrous SO_2 (5.0 mL, liquid) was added at -196 °C. The reaction mixture was warmed to the melting point of SO_2 (-64 °C). After the SO_2 had partially melted and the slurry of reactants was gently agitated, a violent reaction took place producing a bright yellow flame. The reactor was quickly quenched with liquid nitrogen. A check for noncondensable gases at -196 °C revealed 9.05 mmol of N_2 as expected for the complete decomposition of 2.267 mmol of N_5N_3 to N_2 . Pumping off all volatiles at -64 °C produced 0.8890 g of a white solid residue (weight expected for 2.267 mmol of $CsSbF_6 = 0.836$ g). The extra weight was due to some residual SO_2 . Raman and infrared spectra of the white solid, after pumping at room temperature, showed it to be pure $CsSbF_6$.

This reaction can be moderated by the separate dissolution of the starting materials in SO_2 and the combination of the resulting clear solutions at -64 °C. Under these conditions, the decomposition reaction proceeded rapidly but without violence and gave the same results as described above.

Reactions of N_5SbF_6 with NaN_3 . To equimolar amounts of NaN_3 and N_5SbF_6 was added CHF_3 as a solvent at -196 °C, and the resulting mixture was warmed to -95 °C and then to -64 °C. No N_2 evolution was observed under these conditions. The CHF_3 was pumped off at -95 °C, and SO_2 was added as a solvent at -196 °C. The mixture was warmed to -64 °C, but again no N_2 evolution was observed. Pumping off the SO_2 at -64 °C resulted in a white solid residue that, based on its room-temperature Raman spectrum, consisted of a mixture of unreacted NaN_3 and N_5SbF_6 , indicating that no reactions had occurred due to the very low solubility of NaN_3 in these solvents.

- (10) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, 1998; p 82.
- (11) Peterson, K. A.; Xantheas, S. S.; Dixon, D. A.; Dunning, T. H., Jr. *J. Phys. Chem. A* **1998**, *102*, 2449. Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154. Dixon, D. A.; Feller, D. *J. Phys. Chem. A* **1998**, *102*, 8209. Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1999**, *110*, 8384. Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 6413. Feller, D. *J. Chem. Phys.* **1999**, *111*, 4373. Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2000**, *104*, 3048. Feller, D.; Sordo, J. A. *J. Chem. Phys.* **2000**, *113*, 485. Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484. Dixon, D. A.; Feller, D.; Sandrone, G. J. *Phys. Chem. A* **1999**, *103*, 4744. Ruscic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. *J. Phys. Chem. A* **2001**, *105*, 1. Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727.
- (12) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
- (13) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- (14) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.
- (15) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (16) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

- (17) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *103*, 1063.
- (18) Christe, K. O.; Wilson, W. W.; Schack, C. J.; Wilson, R. D. *Inorg. Synth.* **1986**, *24*, 39.

Computational Approaches

Enthalpies of Formation. The augmented correlation consistent basis set aug-cc-pVnZ ($n = D, T, Q$)¹⁹ was used for nitrogen. Only the spherical components (5-*d*, 7-*f*, 9-*g* and 11-*h*) of the Cartesian basis functions were used. This family of basis sets contains an additional shell (e.g., spd for DZ) of diffuse functions that are necessary for an accurate description of anions. Calculations were performed using the MOLPRO,²⁰ Gaussian,²¹ and GAMESS²² suites of programs. The open shell CCSD(T) calculations were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree–Fock (ROHF) calculation was initially performed to generate the set of molecular orbitals and the spin constraint was relaxed in the coupled cluster calculation.^{23–25} The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form:

$$E(n) = E_{\text{CBS}} + A \exp[-(n-1)] + B \exp[-(n-1)^2] \quad (1)$$

with $n = 2$ (aug-cc-pVDZ), 3 (aug-cc-pVTZ), etc., as first proposed by Peterson et al.²⁶ This extrapolation method has been shown to yield atomization energies in the closest agreement with experiment by a small measure as compared to other extrapolation approaches up through $n = 4$.⁸

Most geometries were optimized at the frozen core CCSD(T) level with various augmented correlation-consistent basis sets. With the exception of the N₅ radical, all geometries were optimized with the aug-cc-pVTZ or aug-cc-pVQZ basis sets. If the CCSD(T)/aug-cc-pVQZ geometry was not available, the CCSD(T)/aug-cc-pVTZ geometry was used for the CCSD(T)/aug-cc-pVQZ calculation. Geometries for the N₅ radicals were obtained from ZAPT2/6-311+G(2df) and CCSD(T)/aug-cc-pVDZ calculations. Vibrational frequencies were calculated at the CCSD(T) and MP2 levels with the aug-cc-pVDZ basis set. Calculations were performed on SGI, IBM, and Apple G4 computers.

Core–valence corrections, ΔE_{CV} , were obtained at the CCSD(T)/cc-pCVTZ level of theory.²⁷ Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass–velocity and 1-electron Darwin (MVD) terms in the Breit–Pauli Hamiltonian.²⁸ Because N has a ⁴S ground state, there are no atomic spin–orbit corrections to the total atomization energies. The spin–orbit coupling

constant for N₃ is 71.3 cm^{−1} based on experiment,²⁹ leading to a spin–orbit correction of 0.10 kcal/mol.

By combining our computed $\sum D_0$ values with the known enthalpies of formation³⁰ at 0 K for N of $\Delta H_f^0(\text{N}) = 112.53 \pm 0.02$ kcal mol^{−1}, we can derive ΔH_f^0 values for the molecules under study in the gas phase. We obtain enthalpies of formation at 298 K by following the procedures outlined by Curtiss and co-workers¹⁶ and by using the stationary electron convention; that is, we do not assume a change in the enthalpy of formation of the electron as a function of temperature.

Lattice Energies. For this study, eq 2³¹

$$U_L = 2I[\alpha V_m^{-1/3} + \beta] \quad (2)$$

was used to estimate the lattice energy, U_L , of the salts N₅⁺N₅[−] and N₅⁺N₃[−] from estimated ion volumes. I is the ionic strength (=1), V_m is the molecular (formula unit) volume of the lattices involved which is equal to the sum of the individual ion volumes of the cation, V_+ , and anion, V_- , and α and β take the values 28.0 kcal mol^{−1} nm and 12.4 kcal mol^{−1}, respectively, for 1:1 salts. The individual ion volumes can be estimated from an ion volume database,³¹ inferred in some cases from established crystal structure data, or calculated. To calculate the volumes of the ions, we chose to use the volumes that we have used in free energy of solvation calculations.³² The electron densities were calculated at the B3LYP/6-31+G* level,³³ and the volume was taken to be that inside the 0.001 au contour of the electron density.

Results and Discussion

Calculated Geometries. The calculated geometries for the molecules, N₂, N₃, N₃[−], N₅[−], and N₅⁺ are summarized in Table 1.

N₂. As expected, the geometry for N₂ at the CCSD(T)/aug-cc-pVQZ level is in excellent agreement with the experimental value.³⁴ Theory overestimates experiment by 0.0028 Å. For comparative purposes, we also optimized the N–N bond length with the larger aug-cc-pV5Z basis set. This produced a small 0.0010 Å decrease in the bond length, indicating that the aug-cc-pVQZ bond lengths should be within approximately 0.001 Å of the basis set limit for the other molecules that could be treated at this level of theory. If the frozen core approximation is removed via calculations with the core/valence (CV) cc-pCVQZ basis set, another 0.0020 Å shortening of the bond length is observed. The final CCSD(T)/aug-cc-pV5Z + CV bond length of 1.0975 Å is almost identical to the experimental value of 1.0977 Å.

N₃. The geometry for N₃ ($D_{\infty h}$) is in excellent agreement with the experimental value.³⁵ The calculations predict a value for the NN bond that is slightly shorter than the experimental value. This result is in contrast to N₂ where the calculations predict a longer bond at the CCSD(T)/aug-cc-pVQZ level.

(19) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(20) MOLPRO is a package of ab initio programs. Werner, H. J.; Knowles, P. J.; Almlöf, J.; Amos, R. D.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Elbert, S. T.; Hampel, C.; Lindh, R.; Lloyd, A. W.; Meyer, W.; Nicklass, A.; Peterson, K. A.; Pitzer, R. M.; Stone, A. J.; Taylor, P. R.; Mura, M. E.; Pulay, P.; Schütz, M.; Stoll, H.; Thorsteinsson, T. *MOLPRO*; Universität Stuttgart and University of Birmingham: Stuttgart, Germany and Birmingham, England, 2000.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, A. C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(22) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(23) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, *92*, 3033.

(24) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1994**, *99*, 5219.

(25) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(26) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.

(27) Peterson, K. A.; Dunning, T. H., Jr. Private communication.

(28) Davidson, E. R.; Ishikawa, Y.; Malli, G. L. *Chem. Phys. Lett.* **1981**, *84*, 226.

(29) Douglas, A. E.; Jones, W. J. *Can. J. Phys.* **1965**, *43*, 2216.

(30) Chase, M. W., Jr. NIST-JANAF Tables, 4th ed. *J. Phys. Chem. Ref. Data*, Mono. 9, **1998**, Suppl. 1.

(31) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609. Jenkins, H. D. B.; Tudela, D.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 2364.

(32) Zhan, C.-G.; Dixon, D. A. *J. Phys. Chem. A* **2001**, *105*, 11534. Zhan, C.-G.; Dixon, D. A. *J. Phys. Chem. A* **2002**, *106*, 9737. Zhan, C.-G.; Bentley, J.; Chipman, D. M. *J. Chem. Phys.* **1998**, *108*, 177. Zhan, C.-G.; Chipman, D. M. *J. Chem. Phys.* **1998**, *109*, 10543.

(33) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(34) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules*; Van Nostrand Reinhold Col, Inc.: New York, 1979; Vol. 4.

(35) Brazier, C. R.; Bernath, F. P.; Burkholder, J. B.; Howard, C. J. *J. Chem. Phys.* **1988**, *89*, 1762.

Table 1. Calculated Valence Correlated Geometries $N_n^{x,a}$

species	basis	r (NN)	θ (NNN)
$N_2(\tilde{X}^1A)$	CCSD(T)/aug-cc-pVDZ	1.1209	
	CCSD(T)/aug-cc-pVTZ	1.1040	
	CCSD(T)/aug-cc-pVQZ	1.1005	
	CCSD(T)/aug-cc-pV5Z	1.0995 ^b	
	expt ³⁴	1.0977	
$N_3(\tilde{X}^2\Pi_g)$	CCSD(T)/aug-cc-pVDZ	1.1997	180.0 ^c
	CCSD(T)/aug-cc-pVTZ	1.1840	
	CCSD(T)/aug-cc-pVQZ	1.1802	
	expt ³⁵	1.18115	
$N_3^-(\tilde{X}^1\Sigma_g^+)$	CCSD(T)/aug-cc-pVDZ	1.2072	180.0 ^c
	CCSD(T)/aug-cc-pVTZ	1.1912	
	CCSD(T)/aug-cc-pVQZ	1.1876	
	expt ³⁶	1.1884	
$N_5^-(\tilde{X}^1A_1')$	CCSD(T)/aug-cc-pVDZ	1.3429	108.0 ^c
	CCSD(T)/aug-cc-pVTZ	1.3309	
$N_5^+(\tilde{X}^1A_1)$	CCSD(T)/aug-cc-pVDZ	1.1319	165.87
	CCSD(T)/aug-cc-pVTZ	1.3413	107.90
	CCSD(T)/aug-cc-pVTZ	1.1159	167.08
	CCSD(T)/aug-cc-pVTZ	1.3238	108.48
	expt ²	1.10	168.1
	expt ²	1.30	111.2
$N_5^2(A_1)^d$	ZAPT2/6-311+G(2df)	1.292	121.0
		1.343	100.1
		1.355	109.5
	CCSD(T)/aug-cc-pVDZ	1.422	102.3
		1.165	137.7
		2.576	81.1
$N_5^- - TS^e$	MP2/aug-cc-pVDZ	1.270	125.5
		1.702	99.4
		1.215	107.8
	CCSD(T)/6-311+G(d) ⁷	1.252	128.9
		1.764	
		1.191	

^a Bond distances in angstroms and bond angles in degrees. ^b Core/valence correlation at the CCSD(T)/cc-pCVQZ level shortens the bond length by 0.0020 Å, resulting in an estimated CCSD(T)/aug-cc-pV5Z+CV value of 1.0975 Å. ^c Constrained by symmetry to these angles. Linear for N_3 and N_3^- and D_{5h} for N_5^+ . ^d The radical is cyclic with the symmetry unique atom N1 at the apex. N1 is bonded to N2 and N5, and N2 is bonded to N3, and N3 is bonded to N4. The bond distances are in the order: $r(N1-N2)$ and $r(N1-N5)$; $r(N2-N3)$ and $r(N4-N5)$; and $r(N3-N4)$. The bond angles are in the order $\angle N2N1N5$; $\angle N1N2N3$ and $\angle N1N5N4$; and $\angle N2N3N4$ and $\angle N5N4N3$. ^e The transition state for the anion decomposition is cyclic with the symmetry unique atom N1 at the apex. N1 is bonded to N2 and N5, and N2 is bonded to N3, and N3 is bonded to N4. The bond distances are in the order $r(N1-N2)$ and $r(N1-N5)$; $r(N2-N3)$ and $r(N4-N5)$; and $r(N3-N4)$. The bond angles are in the order $\angle N2N1N5$; $\angle N1N2N3$ and $\angle N1N5N4$; and $\angle N2N3N4$ and $\angle N5N4N3$.

N_3^- . The calculated geometry for N_3^- is also in very good agreement with experiment, with the calculated NN bond length again being slightly shorter than experiment.³⁶

N_5^+ . The geometry for N_5^+ has been measured in the crystal by X-ray diffraction techniques.² The calculated values are in good agreement with the crystal structure values considering the uncertainty in the experimental values and the different environment. The calculated geometrical parameters for N_5^+ are the same as those reported by Fau and Bartlett at the CCSD(T)/aug-cc-pVTZ level,⁵ whereas the geometries calculated for N_3^- at the same level differ slightly.

N_5^- . The value of 1.334 Å calculated for the NN bond length in N_5^- at the CCSD(T)/6-311+(G(d,p)) level⁷ lies between our values calculated at the CCSD(T) level with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively.

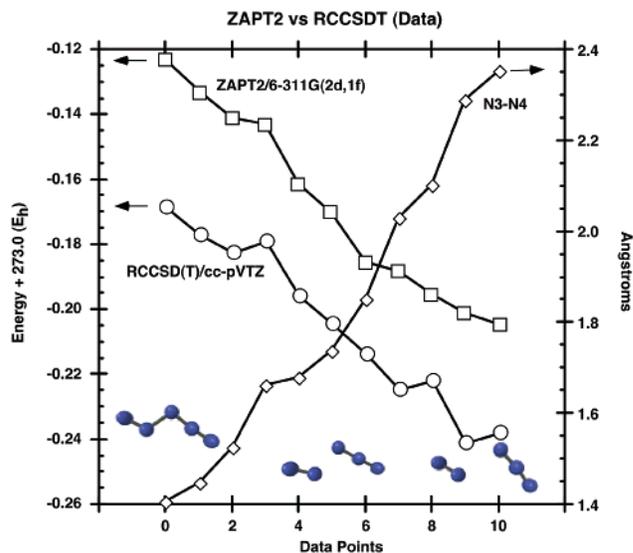


Figure 1. Schematic showing the decomposition of the N_5 radical formed by electron attachment to N_5^+ at the ZAPT2/6-311G(2d,f) and CCSD(T)/cc-pVTZ levels. The radical smoothly dissociates to products. The x axis corresponds to the calculation number describing the dissociation, and the y axis corresponds to the energy or to the N3–N4 (numbered starting from the right) interaction distance representing the separation between the N_2 and N_3 molecules. The large squares correspond to the ZAPT/6-311G(2d,-1f) potential energy surface, and the circles correspond to the CCSD(T)/cc-pVTZ potential energy surface. The small squares represent the N3–N4 distance which increases.

N_5 (Open Isomer). ZAPT2³⁷ calculations with the 6-311+G-(2df) basis set followed by CCSD(T)/cc-pVTZ single-point calculations confirm previous conclusions⁷ that the N_5 radical starting from this geometry is vibrationally unstable. Starting from the optimized N_5^+ structure, the neutral species dissociates without a barrier to $N_3 + N_2$ as shown in Figure 1.

N_5 (Cyclic Isomer). The N_5 radical cyclic isomer would be generated by detaching an electron from cyclic N_5^- . The HOMO of N_5^- is a degenerate in-plane orbital involving essentially lone pair interactions. Production of the N_5 radical leads to (e)³ occupancy which Jahn–Teller distorts to a C_{2v} structure. Two states can be derived from the (e)³ occupancy, a 2A_1 state and a 2B_1 state (a 2B_2 state would be a π radical). The geometry for the cyclic N_5 (C_{2v}) 2A_1 radical was found to be a stationary point on the ZAPT2/6-311+G(2df) potential energy surface. The cyclic N_5 radical at the ZAPT2/6-311+G(2df) geometry is 66.8 kcal/mol above the $N_3 + N_2$ asymptote at the CCSD(T)/cc-pVTZ level. The longest NN ZAPT/6-311+G(2df) bond distance is that in the base of the pentagon, 1.354 Å. The shortest NN bonds are those connected to the apex, 1.292 Å. We took this geometry and initiated an optimization at the R/UCCSD(T)/aug-cc-pVDZ level for both the 2A_1 and the 2B_1 states under the constraint of C_{2v} symmetry. The 2B_1 state smoothly dissociated to the $N_3 + N_2$ asymptote, showing that on the CCSD(T)/aug-cc-pVDZ surface, this state is not a minimum. The N_3 distance converges faster than the N_2 distance. The 2A_1 state is difficult to optimize but finally optimizes to a structure with two elongated N_2 molecules complexed weakly to an N atom (see Table 1), as it cannot go to the products $N_2 + N_3$. At the CCSD(T)/aug-cc-pVTZ level using the optimized CCSD-

(36) Polak, M.; Gruebele, M.; Saykally, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2884.

(37) Fletcher, G. D.; Gordon, M. S.; Bell, R. S. *Theor. Chem. Acc.* **2002**, *107*, 57.

(T)/aug-cc-pVDZ geometry, the 2A_1 state is 60.2 kcal/mol above the $N_2 + N_3$ asymptote. These calculations strongly suggest that, on electron detachment from N_5^- , the resulting radical has a path on the 2B_1 surface that leads directly to the $N_3 + N_2$ asymptote and that there is no stable cyclic N_5 radical structure, as has already been noted previously.⁷ As part of a study of $Fe(\eta^5-N_5)_2$, Frenking and co-workers reported a structure for the 2A_1 state of the N_5 radical at the B3LYP/6-31G(d) level which could be a minimum, although the structure was not discussed.³⁸ Our result is also consistent with the prediction⁷ of Nguyen and Ha that cyclic N_5 is not stable with respect to dissociation.

Calculated Frequencies. The calculated vibrational frequencies for N_2 , N_3 , N_3^- , N_5^- , N_5 (cyclic), and N_5^+ are summarized in Table 2.

N_2 . The harmonic frequency at the frozen core CCSD(T)/aug-cc-pVQZ level is within 5 cm^{-1} of the experimental value.³⁴ Even at the CCSD(T)/aug-cc-pVTZ level, the N_2 frequency is within 20 cm^{-1} , and, at the CCSD(T)/aug-cc-pVDZ level, it is within 40 cm^{-1} . This level of agreement is in part fortuitous. Whereas the aug-cc-pV5Z basis set frequency is identical to the experimental value, introduction of core/valence correlation increases ω_e by 9.2 cm^{-1} . Thus, the final CCSD(T)/aug-cc-pV5Z + CV value is 9 cm^{-1} larger than experiment.

N_3 . For N_3 , the frequencies calculated at the MP2/aug-cc-pVDZ level are in qualitative agreement with the experimental values³⁹ for the π bend and the symmetric stretch and in good agreement for the antisymmetric stretch. In this case, we have used the experimental frequencies to calculate the zero-point energy.

N_3^- . For N_3^- , the calculated antisymmetric harmonic stretch is in excellent agreement with the gas-phase experimental value.^{35,40} The value for the ν_2 bending frequency for this ion has been measured in the solid state, and a free space estimate for ν_1 has been obtained based on the spectrum measured for the solid.^{41,42} For this ion, we used the experimental frequencies for the zero-point energy determination. Use of the theoretical frequencies introduces a difference of 0.19 kcal/mol because the calculated bend and antisymmetric stretch are ~ 50 cm^{-1} lower than the experimental values. The frequencies calculated by us for ν_1 and ν_3 are in reasonable agreement with those previously calculated at the CASPT2 level¹⁷ and at the CEPA level.⁴²

N_5^- . For this ion, we used the frequencies calculated at the CCSD(T)/aug-cc-pVDZ level for the zero-point energy calculation as there are no experimental values available. Quite good agreement is found for the frequencies of N_5^- calculated at the MP2/aug-cc-pVDZ level and at the CCSD(T)/aug-cc-pVDZ level. The CASPT2 frequencies¹⁷ are similar to our values.

N_5 (Cyclic Isomer). Frequencies were calculated at the ZAPT2/6-311+G(2df) level of theory for the 2A_1 state. No experimental values are available for this species. As noted above, the 2B_1 structure is not a minimum for the cyclic radical at the R/UCCSD(T)/aug-cc-pVDZ level.

Table 2. Calculated Valence Correlated Harmonic Vibrational Frequencies (cm^{-1})

method	mode number	mode symmetry	mode description	ω	expt
N_2					
CCSD(T)/aug-cc-pVDZ	1	σ_g	N_2 str	2319	2331 ^a (2358.6)
CCSD(T)/aug-cc-pVTZ	1	σ_g	N_2 str	2340	
CCSD(T)/aug-cc-pVQZ	1	σ_g	N_2 str	2354	
CCSD(T)/aug-cc-pV5Z	1	σ_g	N_2 str	2359 ^b	
N_3					
MP2/cc-pVTZ	1	π	bend ^b	594	457 ^c
	2	σ_g	symmetric str	1434	1320 ^c
	3	σ_u	asymmetric str	1620	1645 ^c
N_3^-					
CCSD(T)/aug-cc-pVDZ	1	π	bend	578	626 ^d
	2	σ_g	symmetric str	1281	1335 ^e
	3	σ_u	asymmetric str	1999	1986 ^f
N_5^-					
CCSD(T)/aug-cc-pVDZ	1	e_1'	NN str	1202	
	2	a_1'	NN str	1141	
	3	e_2'	NN str	1078	
	4	e_2''	bend	1001	
	5	e_2''	bend	739	
MP2/aug-cc-pVDZ	1	e_1'	NN str	1143	
	2	e_2'	NN str	1123	
	3	a_1'	NN str	1094	
	4	e_2''	bend	1039	
	5	e_2''	bend	740	
N_5^+					
MP2/aug-cc-pVDZ	1	b_2	NN str	2260	2267 ^g
	2	a_1	NN str	2179	2206 ^g
	3	b_2	NN str	1199	1064 ^g
	4	a_1	NN str	881	870 ^g
	5	a_1	bend	669	671 ^g
	6	b_2	bend	431	414 ^g
	7	a_2	out-of-plane bend	426	474 ^g
	8	b_1	bend	374	421 ^g
	9	a_1	bend	179	204 ^g
N_5^--TS					
MP2/aug-cc-pVDZ	1	b_2	NN str	1649	
	2	a_1	NN str	1572	
	3	a_1	NN str	1244	
	4	a_1	NN str	905	
	5	b_2	bend	848	
	6	b_1	bend	684	
	7	a_2	out-of-plane bend	591	
	8	b_2	bend	182	
	9	a_1	NN str	862i	
N_5 (cyclic) 2A_1					
ZAPT2/6-311+G(2df)	1	b_2	NN str	1221	
	2	a_1	NN str	1147	
	3	a_1	NN str	1064	
	4	b_2	NN str	1033	
	5	a_1	NN str	1002	
	6	a_1	bend	843	
	7	b_2	bend	798	
	8	a_2	out-of-plane bend	729	
	9	b_1	bend	363	

^a Reference 34. Value in parentheses is the harmonic value. ^b Core/valence correlation at the CCSD(T)/cc-pCVQZ level of theory increases the harmonic frequency by 9.2 cm^{-1} , resulting in an estimated CCSD(T)/aug-cc-pV5Z+CV value of 2368 cm^{-1} . ^c Reference 39. ^d Lamoureux, R. T.; Dows, D. A. *Spectrochim. Acta, Part A* **1975**, *31*, 1945. From N_3^- in a KI lattice. ^e References 41 and 42. ^f Reference 36. ^g Reference 2. ^h Average of 565 and 622 cm^{-1} .

N_5^+ . For N_5^+ , there is reasonable agreement between the frequencies calculated at the MP2/aug-cc-pVDZ level and the average of the frequencies taken from measurements in the solid state.² The largest discrepancy is found for the highest frequency b_2 mode with a difference of ~ 140 cm^{-1} . The calculated a_2 and b_1 modes deviate by ~ 50 cm^{-1} from the experimental values. The fact that the differences cancel out leads to

(38) Lein, M.; Frunzke, J.; Timoshkin, A.; Frenking, G. *Chem.-Eur. J.* **2001**, *7*, 4155.

(39) Jacox, M. E. *J. Phys. Chem. Ref. Data* **1994**, Monograph No. 3.

(40) Polak, M.; Gruebele, M.; Saykally, R. J. *J. Chem. Phys.* **1988**, *89*, 110.

(41) Sherman, W. F.; Wilkinson, G. R. In *Vibrational Spectroscopy of Trapped Species*; Hallam, H. E., Ed.; Wiley: London, 1973.

(42) See for a quoted value for ν_1 : Botschwina, P. *J. Chem. Phys.* **1986**, *85*, 4591.

Table 3. Contributions to the Total Energy for N_x^m and Relative Energies

contribution ^a	N (⁴ S)	N ₂ (¹ Σ ⁺)	N ₃ (² Π)	N ₃ ⁻ (¹ Σ ⁺)	N ₅ ⁻ (¹ A ₁)	N ₅ ⁺ (¹ A ₁)	N ₅ -TS (¹ A ₁) MP2	N ₅ -TS (¹ A ₁) ref 7 geom
aug-cc-pVDZ ^b	-54.486849	-109.295320	-163.770896	-163.863661	-273.142269	-272.683885	-273.101846	-273.099657
aug-cc-pVTZ ^b	-54.516714	-109.380845	-163.900633	-163.997758	-273.360072	-272.900359	-273.317071	-273.315909
aug-cc-pVQZ ^b	-54.525300	-109.407243	-163.939895	-164.038815	-273.428772	-272.965446	-273.383465	-273.382442
Est. CBS eq 1 ^c	-54.530069	-109.422126	-163.961942	-164.061926	-273.467671	-273.001946	-273.420892	-273.419928
ΔE _{elec} CBS eq 1 ^d		227.15	233.26	296.00	512.87	220.63	483.52	482.91
ΔE _{CV} ^e		0.65	1.03	1.22	1.66	1.80		
ΔE _{SR} ^f		-0.11	-0.51	-0.51	-1.04	-0.85		
ΔE _{ZPE} ^g		-3.35	-5.54	-6.53	-13.12	-12.27	-10.96	-10.0
ΣD ₀ ^h		224.34	228.34 ^k	290.18	500.37	209.31		
ΔH _f (0 K) ⁱ	112.53	0.72	109.25	47.41	62.28	353.34		
ΔH _f (0 K) expt		0.0 ³⁰	99.7 ± 5 ³⁰	48 ± 2				
			112 ± 5 ^{43,44}					
ΔH _f (298 K) ^j		0.76	108.6	47.4	59.6	351.6		

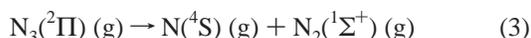
^a Total energies in hartrees and energy differences in kcal/mol. ^b Valence electron only CCSD(T) total energy with the given basis set. Open shell systems were treated with the R/UCCSD(T) method. ^c Estimated frozen core, complete basis set energy obtained from eq 1 using the CCSD(T)/aug-cc-pVxZ (x = D, T, Q) energies. For the sake of comparison, the CBS dissociation energy of N₂ with the aug-cc-pVTZ through aug-cc-pV5Z basis sets is 226.63 kcal/mol. ^d Valence electron atomization energy from extrapolated total energies obtained with eq 1. ^e Core/valence correction obtained from R/UCCSD(T)/cc-pCVTZ calculations. ^f Scalar relativistic correction obtained from CISD/cc-pVTZ calculations. ^g Zero-point vibrational energy contribution. ^h ΣD₀ = ΔE_{elec} + ΔE_{CV} + ΔE_{SR} + ΔE_{SO} + ΔE_{ZPE}. ⁱ Enthalpy of formation at 0 K. ^j Enthalpy of formation at 298 K. ^k Spin-orbit correction of +0.10 kcal/mol for N₃.

calculated and experimental zero-point energies that are essentially identical. We used the average experimental values in our zero-point energy calculations. Our calculated frequencies are in qualitative agreement with those calculated at the CCSD(T)/6-311+G(2d) and B3LYP/6-311+G(2d) levels.^{1,2} The CCSD(T) values are in general lower than our MP2 values except for the a₂ and b₁ modes which are higher. The CASPT2 frequencies differ from ours more than might be expected, especially for the two highest modes.¹⁷

Calculated Enthalpies of Formation. The total atomization energies are given in Table 3. The ΔH_f⁰ values were converted to 298 K following the procedure of Curtiss and co-workers.¹⁶

N₂. As shown in Table 3, the error in the atomization energy of N₂ is 0.76 kcal mol⁻¹ when compared to experiment.³⁰ This leads to an error in the calculated enthalpy of formation at 0 K of 0.76 kcal mol⁻¹. We can thus estimate that the error bars in our heats of formation are likely to be on the order of ±1 kcal/mol.

N₃. The enthalpy of formation of N₃ has been reported by a number of authors. The NIST value³⁰ of 100 ± 5 kcal mol⁻¹ at 0 K is almost 10 kcal mol⁻¹ below our calculated value. Our calculated value of 109.2 kcal mol⁻¹ is in much better agreement with the value of 112 ± 5 based on the experimental measurement of the acidity of HN₃ and the measurement of the electron affinity of N₃⁻.^{43,44} Our value of 109.25 kcal mol⁻¹ is in excellent agreement with the scaled value of 109.25 kcal mol⁻¹ given by Martin et al.⁸ The calculated atomization energies show that reaction 3



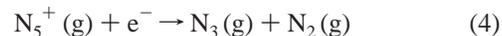
is only 4 kcal mol⁻¹ endothermic at 0 K.

N₃⁻. The enthalpy of formation of N₃⁻ has been determined from gas-phase acidity measurements and the enthalpy of formation of HN₃ to be 48 ± 2 kcal mol⁻¹.⁴³ This value is in excellent agreement with our calculated value of 47.2 kcal

mol⁻¹. Fau and Bartlett calculated the enthalpy of formation of N₃⁻ by a variety of methods.⁵ Their best estimated enthalpy of formation of 47.8 kcal mol⁻¹ is in good agreement with our value. The electron affinity of N₃ has been measured to be 2.68 ± 0.01 eV.⁴⁴ Our calculated adiabatic electron affinity of 2.69 eV is in excellent agreement with this result. With an ANO (4s3p2d1f) basis set, the CASPT2 electron affinity was predicted to be 2.64 eV.¹⁷

N₅⁺. The enthalpy of formation of N₅⁺, calculated by us, is 353.4 kcal mol⁻¹. This result is in reasonable agreement with the value of 347.1 kcal mol⁻¹, calculated by Fau and Bartlett.⁵ Christe and co-workers^{1,2} predicted the enthalpy of formation of N₅⁺ to be 351.1 kcal mol⁻¹ at the CCSD(T) level with a polarized double-ζ basis set. Nguyen and Ha predict a heat of formation of 351.3 ± 3.6 kcal/mol based on CCSD(T)/6-311+G(3df) calculations and the experimental energy of N₃.⁷

The adiabatic electron affinity of N₅⁺ is given by the energy difference between its enthalpy of formation and those of the first metastable neutral reaction or decomposition products. Because the intermediate, open-chain N₅ radical, formed by the addition of an electron to N₅⁺, is unstable and spontaneously dissociates to N₃(g) + N₂(g), the energy of reaction 4 provides the adiabatic electron affinity of N₅⁺.



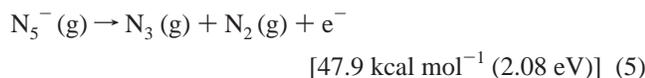
The N₃ radical and N₂ only form a weakly bound van der Waals complex with a binding energy on the order of less than 1 kcal mol⁻¹. Our calculated value of 243.3 kcal mol⁻¹ (10.55 eV) for reaction 4 is much higher than either the vertical electron affinity of 6.04 eV reported by Fau et al.⁵ or the adiabatic ionization energy of 7.4 ± 0.2 eV reported by Nguyen and Ha,⁷ but is in excellent agreement with our experimental bracketing study² that showed the electron affinity of N₅⁺ to fall between 10.52 and 11.48 eV.

N₅⁻. The enthalpy of formation of N₅⁻ is calculated to be 62.2 kcal mol⁻¹, in excellent agreement with the value of 62.1 ± 3.6 kcal/mol given by Nguyen and Ha.⁷ This value can be used to calculate the adiabatic ionization potential of N₅⁻ in the same manner as discussed above for N₅⁺. As noted above, loss of an electron from the degenerate HOMO of N₅⁻ leads to

(43) Pellerite, M. J.; Jackson, R. L.; Brauman, J. I. *J. Phys. Chem.* **1981**, *85*, 1624.

(44) Illenberger, E.; Comita, P. B.; Brauman, J. I.; Fenzlaff, H. P.; Heni, M.; Heinrich, N.; Koch, W.; Frenking, G. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1026. Jackson, R. L.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 1802.

either a 2B_1 or a 2A_1 radical. We have shown that formation of the 2B_1 radical provides a pathway leading to $N_3 + N_2$, so the following channel (reaction) represents the adiabatic ionization process:



Use of this channel gives an adiabatic ionization potential of 2.08 eV for N_5^- . Because of the dissociative nature of the cyclic N_5 radical, this is the most appropriate value to use in the Born–Haber cycles discussed below.

The important dissociation channel for N_5^- is the formation of $N_3^- + N_2$. We predict this channel to be exothermic by 14.2 kcal mol $^{-1}$ at 0 K. This value is in good agreement with the value of 14.3 kcal mol $^{-1}$ reported by Nguyen and Ha at the CCSD(T)/aug-cc-pVTZ level.⁷ It is important to know if there is a barrier separating N_5^- from the asymptotic products N_3^- and N_2 . Nguyen and Ha calculated the energy barrier to dissociation as 27.7 kcal mol $^{-1}$ at the CCSD(T)/aug-cc-pVTZ level including zero-point corrections based on a geometry calculated at the CCSD(T)/6-311+G(d) level.⁷ We have calculated the energy of the transition state at the CCSD(T)/CBS level with Nguyen and Ha's geometry and with the geometry optimized by us at the MP2/aug-cc-pVDZ level. We calculated the geometry at the latter level to get a value of the zero-point energy as well as the value of the imaginary frequency characterizing the transition state. The results are given in Tables 1–3. Our calculated energy barrier using the MP2 geometry is 29.4 kcal mol $^{-1}$, and when the zero-point energy difference is included, the barrier is 27.2 kcal mol $^{-1}$. The energy barrier using the Nguyen and Ha geometry is 0.61 kcal mol $^{-1}$ higher in energy than our value based on the MP2 geometry, showing that the two geometries give essentially identical barrier heights. The barrier calculated⁷ by Nguyen and Ha is very similar to our CCSD(T)/CBS value using their geometry. At the CASPT2/ANO(4s3p2d) level, the barrier is predicted to be 26 kcal mol $^{-1}$, and the dissociation energy to N_3^- and N_2 is predicted to be exothermic by 9 kcal mol $^{-1}$,¹⁷ 5 kcal mol $^{-1}$ lower than our value. A calculation of the imaginary frequency for the transition state of the N_5^- decomposition shows a large value of 862i cm $^{-1}$, suggesting that the ion might be able to tunnel through the barrier to reach the products. We can make a crude estimate of the tunneling effect by using the Wigner expression.⁴⁵ This leads to an enhancement of the dissociation rate by 1.7 at 298 K. This suggests that tunneling should be considered when predicting the stability of N_5^- . For lower temperatures, a larger tunneling effect would be expected.

The origin of the difference between the vertical and the adiabatic potentials, of course, is the dissociation energy of neutral N_5 to N_3 and N_2 . Vertical electron affinities or ionization potentials for the ionic systems under study correspond to removal or addition of an electron to the ion to form a radical at the geometry of the ion. Only when the neutral radicals are vibrationally stable species with geometries similar to those of the starting materials will their vertical EA or IP values approximate the adiabatic values. If this is not the case, the

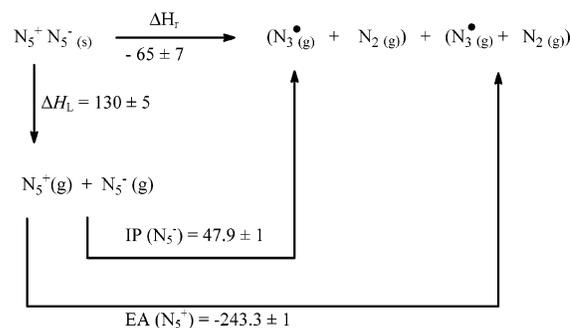


Figure 2. Born–Haber cycle in kcal mol $^{-1}$ for the decomposition reaction of solid $N_5^+N_5^-$. The large negative value for ΔH_f demonstrates the unlikelihood of this salt to exist.

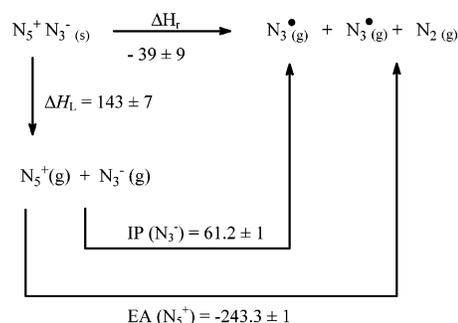


Figure 3. Born–Haber cycle in kcal mol $^{-1}$ for the decomposition reaction of solid $N_5^+N_3^-$. The large negative value for ΔH_f demonstrates that this salt is also unlikely to exist.

radicals generated by the neutralization process spontaneously undergo further decomposition. If these decompositions to the first well-defined, vibrationally stable products do not involve any significant activation energy barriers and if they occur on a fast time scale, it is appropriate to add their energies to the vertical potentials.

Lattice Energy Calculations. Prediction of lattice energies, U_L , based on eq 2 requires an estimate of the relevant ion volumes and gives the following results:

$N_5^+N_3^-$. $V(N_5^+)$ is estimated to be 0.051 (± 0.020) nm 3 based on the reported² crystal structure volume for $N_5^+Sb_2F_{11}^-$ by subtraction of $V(Sb_2F_{11}^-)$ (Table 6, ref 31). $V(N_3^-)$ is equal to 0.058 (± 0.014) nm 3 (Table 5, ref 31), and thus $V(N_5^+N_3^-) = 0.109$ (± 0.024) nm 3 , leading to an estimate for $U_L(N_5^+N_3^-) = 142$ (± 7) kcal mol $^{-1}$.

$N_5^+N_5^-$. An upper limit for $V(N_5^-)$ can be estimated from consideration of $V(N_2)$ and $V(N_3^-)$. The volume of solid dinitrogen, $V(N_2)$, which is dimorphous,⁴⁶ can be obtained from crystal structure data for the α -cubic and the hexagonal forms and averages to $V(N_2) = 0.046$ (± 0.001) nm 3 , leading to $V(N_5^+N_5^-) = 0.155$ (± 0.014) nm 3 , giving a value for $U_L(N_5^+N_5^-) = 129$ (± 5) kcal mol $^{-1}$. Alternatively, we can estimate the volume of the ions at the B3LYP/6-31+G* level as described above: $V(N_5^+) = 0.068$ nm 3 ; $V(N_5^-) = 0.088$ nm 3 , $V(N_3^-) = 0.065$ nm 3 . These estimated volumes yield $U_L(N_5^+N_5^-) = 129$ kcal mol $^{-1}$ and $U_L(N_5^+N_3^-) = 135$ kcal mol $^{-1}$, well within the above error limits. The corresponding lattice enthalpies, ΔH_L , appropriate for use in the cycles of Figures 2 and 3 are $U_L(N_5^+N_5^-) + 2RT$ and $U_L(N_5^+N_3^-) + {}^3/2RT$, respectively.

Stability Predictions Based on Born–Haber Cycles. For a chemical reaction to be thermodynamically favorable, its free

(45) Johnston, H. S. *Gas-Phase Reaction Rate Theory*; Ronald Press: New York, 1966. Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1989.

(46) Landolt, B. *Crystal Structure Data for Inorganic Compounds*; Springer-Verlag: Berlin, 1993.

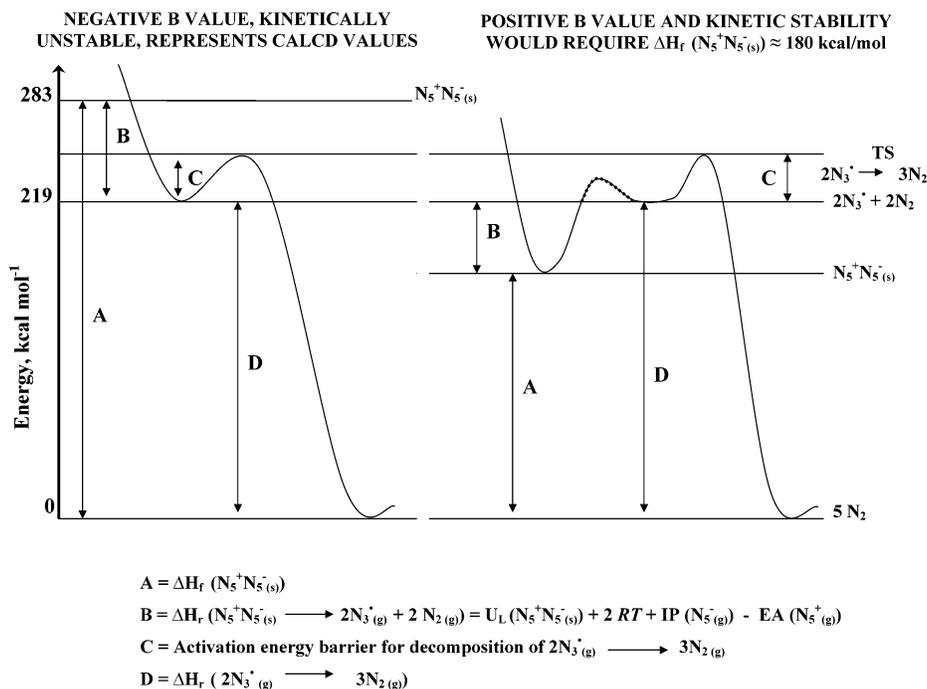
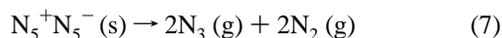


Figure 4. Potential energy curves in kcal mol⁻¹ for the decomposition reaction of solid $N_5^+N_5^-$ to dinitrogen. The left curve is based on the calculated values from this study and shows that a hypothetical $N_5^+N_5^-$ would spontaneously decompose to $2N_3(g) + 2N_2(g)$. The right curve shows that for $N_5^+N_5^-$ to be stable, its enthalpy of formation would have to be significantly lower than those of the gaseous species ($2N_3 + 2N_2$). The broken line indicates that the barrier might possibly exceed the B value.

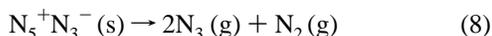
energy change must be zero or negative. If the reaction involves a barrier, a sufficient amount of activation energy must be supplied to overcome this barrier. If the reaction does not have an activation energy barrier, a spontaneous reaction occurs when its free energy change becomes negative. An example of such a reaction is the dissociation of an ionic solid into two radicals (reaction 6), assuming that the electron transfer from the cation to the anion proceeds without a barrier.



If $A(g)$ and $B(g)$ are kinetically stable species possessing an activation energy barrier toward further decomposition, the stability of solid A^+B^- is determined solely by the sum of the adiabatic electron affinity of A^+ , the adiabatic first ionization potential of B^- , and the lattice energy of solid A^+B^- . If, however, the radicals A and B are vibrationally unstable and undergo further spontaneous decomposition without a barrier, then the energies of the first vibrationally stable decomposition products must be used in place of those of $A(g)$ and $B(g)$. This is the case for $N_5^+N_5^-$, where both the open and the cyclic N_5 radicals are vibrationally unstable. Therefore, the decomposition of $N_5^+N_5^-(s)$ is given by reaction 7, and the corresponding Born–Haber cycle is shown in Figure 2.



Those for $N_5^+N_3^-(s)$ are given by eq 8 and Figure 3.



The values shown in the Born–Haber cycles of Figures 2 and 3 are enthalpies. Because the stabilities of the compounds depend on the free energy changes and not the enthalpy changes, the entropy contributions from the $T\Delta S$ term to the free energy

must also be included. For the reactions considered in this paper, these contributions are always negative. We can estimate the entropy changes for reactions 7 and 8 as follows. The entropy for the solid is not known, but we can use the entropies of $NH_4^+NO_3^-$ and $NH_4^+N_3^-$, which are 36 and 27 cal/mol K,⁴⁷ respectively, to estimate the value for the N_5^+ salts. Given the well-established entropies of N_2 and N_3 of 45.8 and 54.1 cal/mol K, respectively, we obtain at 298 K for reaction 7 $-T\Delta S = -49$ kcal/mol, if the entropy of $NH_4^+NO_3^-$ is used to estimate that of the solid, and $-T\Delta S = -51$ kcal/mol, if the entropy of $NH_4^+N_3^-$ is used. For reaction 8, the respective values are $-T\Delta S = -35$ and -38 kcal/mol at 298 K. Thus, significantly positive reaction enthalpy values would be required for the compensation of the large negative entropy contributions and the stabilization of $N_5^+N_5^-$ and $N_5^+N_3^-$. A positive ΔG_r value represents the minimum dissociation energy barrier, but one should keep in mind that the actual barrier can well be higher. If, however, the ΔG_r change is negative, spontaneous decomposition occurs in the absence of a significant reaction barrier. The potential energy curves for both scenarios are depicted in Figure 4 for $N_5^+N_5^-$.

The left curve of Figure 4 represents the case of the enthalpy of reaction 7 being negative and having no significant activation energy barrier. It results in spontaneous decomposition of the solid to the first vibrationally stable intermediates, that is, N_3 radicals and N_2 . The right curve of Figure 4 represents the scenario of a positive reaction enthalpy, the only condition under which solid $N_5^+N_5^-$ might exist. This, however, is a hypothetical case, requiring the enthalpy of formation of $N_5^+N_5^-$ to be about 100 kcal mol⁻¹ more negative than the calculated value. Because the values for the IP of N_5^- and the EA of N_5^+ are fixed, the lattice energy of $N_5^+N_5^-$ would have to be about 100 kcal/mol

(47) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, L.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Supplement No. 2.

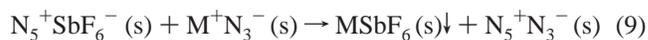
higher than our calculated value, which is impossible based on the molar volumes of the ions involved. The relatively small uncertainties in our ΔH_f values, -65 ± 7 kcal mol $^{-1}$ for $N_5^+N_5^-$ and -39 ± 9 kcal mol $^{-1}$ for $N_5^+N_3^-$, together with the large $-T\Delta S$ terms, allow us to predict with confidence that both compounds cannot be stabilized in the form of ionic solids.

The potential energy surface for N_5^+/N_5^- is quite complicated. The asymptotic energy of $N_5^+ + N_5^-$ is 416 kcal/mol above that of $5N_2$ molecules at 0 K. Our approach to the ion pair energy provides an estimate of 297 kcal/mol above $5N_2$, in good agreement with the Fau et al.⁶ value of 296 kcal/mol. The highly endoergic heat of formation means that the complex is metastable as are all polynitrogen compounds. Thus, there may be a number of decomposition paths.⁴⁸ Neither the N_5 radical derived from N_5^+ at the cation geometry nor the N_5 radical derived from N_5^- at the anion geometry are stable species as shown above. These two N_5 species are doublets, and hence there can be both a triplet coupling and a singlet coupling of the two unpaired electrons after the electron transfer process. The singlet coupling, if the geometries remain similar to the parent ion geometries, should generally be considered as an open shell singlet, not necessarily restricted to a closed shell description.⁶ Enforcing singlet closed shell (i.e., RHF) pairing in the ground-state wave function prevents the two N_5 species from coming apart as N_5 radicals (or their dissociative products N_2 and N_3) even though the product formation of $2N_3 + 2N_2$ is more than 80 kcal/mol exothermic. On the other hand, the triplet surface could lead to direct dissociation. Including the open shell-singlet paired configuration in a more general multiconfigurational wave function may have the same result. To further study the N_5^+/N_5^- ion pair potential surface, we optimized the lowest $^3A'$ and $^3A''$ states at the ROHF/6-31+G(d) (restricted open shell Hartree-Fock) level, and the lowest $^1A'$ and $^1A''$ states using TCSCF (two-configuration self-consistent field) wave functions and the same 6-31+G(d) basis set. For both spin states, the lower energy state is A' . Geometry optimization of the $^3A'$ state (lowest energy triplet at this level of theory) leads to a large separation of the anion and cation, with a concomitant decrease in the charges on the two species to nearly zero. So, the lowest energy triplet is clearly on its way to dissociation to two radicals, and subsequently to N_2 and N_3 . The other three states (two singlets and one triplet) do not appear to dissociate at these levels of theory. The $^3A'$ state is about 40 kcal/mol above the $^1A'$ state but is still ~ 80 kcal/mol below the separated ion pair dissociation asymptote, showing that there is an electron transfer step leading to dissociation that occurs significantly below the energy of the separated ions. Higher levels of theory may alter these results, and we did not further explore the barriers to dissociation. These results and those of other workers do show that the potential energy surface is very complicated and that there are many potential highly exothermic paths leading to formation of N_3 and/or N_2 . In addition, we note

(48) The energy of the $N_7 + N_3$ channel is 324 kcal/mol above $5N_2$ molecules using the G3 heat of formation of N_7 , and thus $N_7 + N_3$ is 27 kcal/mol above the $N_5^+N_5^-$ ion pair.⁴⁹ The barrier⁶ to form $N_7 + N_3$ from N_5^+/N_5^- is very similar to the endothermicity of the reaction, and this process again involves two open shell molecules. A closed shell asymptote of geometry similar to that of the end-on addition of N_5^+ to N_5^- is $N_8 + N_2$, which is 230 kcal/mol above $5N_2$ at the CCSD(T)/6-311G*/MP2/6-31G* level⁵⁰ and, thus, substantially downhill from the ion pair by ~ 67 kcal/mol. The N_8 molecule that is formed, azidopentazole, has a barrier to formation of $4N_2$ of only 13–14 kcal/mol at the CCSD(T)/6-311G* level⁴⁹ and 19 kcal/mol at the CASPT2/ANO-4s3p2d1f level.⁵¹

that all of these comparisons are at 0 K and that at higher temperatures, there is a significant entropic effect favoring formation of N_2 and N_3 . These results are all consistent with our conclusion that formation of a stable N_5^+/N_5^- ion pair is unlikely, so it cannot be isolated.

Experimental Results and their Comparison with the Predictions. All of our attempts to prepare solid $N_5^+N_3^-$ by the metathesis reaction 9 failed.



In liquid SO_2 , the $N_5^+SbF_6^-$ salt is highly soluble. Using very soluble (solubility at -64 °C = 3.14×10^{-3} mol mL $^{-1}$) CsN_3 , violent reactions occurred resulting in quantitative formation of poorly soluble (solubility at -64 °C = 6.56×10^{-6} mol mL $^{-1}$) $CsSbF_6$ and $4N_2$. Using poorly soluble (solubility at -64 °C = 9.23×10^{-5} mol mL $^{-1}$) NaN_3 , the metathesis did not proceed to any measurable extent, and unreacted NaN_3 and $N_5^-SbF_6$ were recovered. It was also shown that solid NaN_3 and $N_5^-SbF_6$ can be mixed as dry powders at room temperature and the Raman spectrum of the mixture can be recorded without evidence of reaction provided that the laser power is kept at a low level. Attempts to carry out the metathesis in CHF_3 solution were also unsuccessful because of the low solubility of the starting materials in this solvent. These experiments show that, in all cases where metathesis took place, only spontaneous decomposition was observed and, thus, confirm the above given theoretical predictions.

These results are consistent with the predictions by us and by Fau and Bartlett⁵ that $N_5^+N_3^-$ will not be stable. Fau and Bartlett⁵ noted that the reaction of N_5^+ and N_3^- does not lead to ion pair formation and that N_5N_3 is a weak complex even on the closed shell singlet energy surface. This structure is located at -149 kcal/mol on the way toward the $2N_3 + N_2$ final products at -182 kcal/mol (energies with respect to the separated ions). Their results suggest that on the triplet coupled surface, and possibly on the multiconfigurational singlet surface, this species will fully dissociate.

Assessment of the Performance of Solid $N_5^+N_5^-$ as a Monopropellant. It was recently suggested^{6,52} that $N_5^+N_5^-$, if it “could be stabilized, would be an ideal monopropellant because its density is nearly twice that of hydrazine while the energy densities (heat of reaction per gram) are comparable.” Indeed, the previous energy density estimate of 2.11 kcal/g for $N_5^+N_5^-$ is close to our estimate of 1.98 kcal/g. However, our energy density estimate for hydrazine is significantly lower. If one assumes its decomposition to proceed according to eq 10,



the maximum energy density of N_2H_4 would be only 1.17 kcal/g.³⁰ The actual value, however, is even lower because there is always some decomposition of NH_3 to N_2 and H_2 .⁵³ Hence, we conclude that the energy densities of $N_5^+N_5^-$ and N_2H_4 differ

(49) Wang, X.; Tian, A.; Wong, N. B.; Law, H.-K.; Li, W.-K. *Chem. Phys. Lett.* **2001**, *338*, 367.

(50) Chung, G.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **2000**, *104*, 5647.

(51) Gagliardi, L.; Evangelisti, S.; Bernhardsson, A.; Lindh, R.; Roos, B. O. *Int. J. Quantum Chem.* **2000**, *77*, 311.

(52) *Nature*, Science Update, May 15, 2002. *Scientific American*, News, May 15, 2002. *Die Welt*, May 15, 2002.

(53) Schmidt, E. W. *Hydrazine and its Derivatives Preparation, Properties, Applications*; John Wiley & Sons: New York, 1984.

by a factor of 2. Based on our molar volume estimates, the density of $N_5^+N_5^-$ is expected to be 1.50 g/cm³. Even so, we agree with the conclusion⁶ that a hypothetical polynitrogen compound, such as $N_5^+N_5^-$, would be an excellent monopropellant for rocket propulsion or explosives, if it could be synthesized in a stable form.

Conclusions

The following conclusions can be drawn from our studies:

(i) Our results quantitatively examine the stability of $N_5^+N_5^-$ and $N_5^+N_3^-$ and show that both compounds are unstable in the solid state.

(ii) Our results show that for Born–Haber cycle based stability estimates for species, such as N_5^+ and N_5^- , which decompose to vibrationally unstable species upon neutralization, it is important to use adiabatic ionization potentials and electron affinities.

(iii) In view of the instability of the N_5 radicals and their strongly exothermic spontaneous decompositions to N_3 radicals and N_2 , both N_5^+ and N_5^- are not good choices for preparing a stable ionic nitrogen allotrope.

(iv) Our results suggest that $N_5^+N_5^-$ would be even more unstable than $N_5^+N_3^-$, because the former would contain two unstable N_5 species after transfer of the electron.

(v) Stability calculations for individual ions or ion pairs may not provide sufficient information for stability predictions. Rigorous Born–Haber cycles, including realistic lattice energy estimates, and an evaluation of the stability of the decomposition products are required to make meaningful predictions.

(vi) Our theoretical predictions concerning the instability of $N_5^+N_3^-$ and the use of the adiabatic electron affinities and ionization potentials are confirmed by extensive experimental studies involving the low-temperature metatheses of $N_5^+SbF_6^-$ with different alkali metal azides in various solvents and the determinations of electron affinities by bracketing methods, respectively.

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