LETTERS TO THE EDITOR

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NOTES

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The heat of formation of HNO

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INTRODUCTION

The HNO molecule is of interest in both combustion and atmospheric chemistry. For example, Guadagnini *et al.*[1,2] have recently presented *ab initio* potential energy surfaces for the three lowest lying electronic states of HNO and then used these in examining several chemical reactions that take place in the combustion of nitrogen containing fuels and in the oxidation of atmospheric nitrogen. We have previously studied the ground state potential energy surface (i.e., stationary points along the HNO↔HON path), vibrational spectrum (using an accurate quartic force field), zero-point energy, and bonding of HNO using coupled-cluster *ab initio* methods.[3–5] HNO is also very interesting because of the unique nature of its bonding characteristics. That is, the potential energy surface is very flat along the H–N bonding coordinate thereby giving unusual harmonic and fundamental vibrational frequencies, and the H–N bond energy is rather weak in comparison to other H–N bond energies. In fact, using experimental heats of formation[6] for HNO, H, and NO, the H– bond energy is computed to be only 49.9 kcal/mol (298 K). However, *ab initio* calculations of isodesmic reaction energies involving HNO, FNO, ClNO, and several other molecules[3] have shown that there is an inconsistency in the experimental heats of formation of the XNO (X=H, F, and Cl) species. Hence the motivation for this study was to determine a very accurate ΔH_f^o value for HNO using state-of-the-art *ab initio* methods. Based on many recent studies (e.g., see Ref. 7 and references therein) it is evident that the singles and doubles coupled-cluster method that includes a perturbational estimate of the effects of connected triple excitations,[8] denoted CCSD(T), in conjunction with large one-particle basis sets should be reliable to better than ±0.8 kcal/mol for this quantity. The computational methodology is described in the next section followed by our results and discussion. Conclusions are presented in the final section.

THEORETICAL APPROACH

The CCSD(T) electron correlation method has been used in all calculations. The open-shell calculations were performed with the restricted Hartree–Fock formalism of Ref. 9. Dunnings's[10] cc-pVDZ, cc-pVTZ, and cc-pVQZ one-particle basis sets have been used for calculations in which only the valence electrons are included in the correlation procedure. The core-correlation effect on the dissociation energy of NO was determined using Martin and Taylor's[11,12] core-correlation one-particle basis. The cc-pVTZ basis includes through *f* functions on the heavy atoms and through *d* functions on H, whereas the cc-pVQZ basis includes through *g* and *f* functions, respectively. The closed-shell coupled-cluster energies were determined with the TITAN[13] coupled-cluster programs interfaced to the SEWARD[14] integral program and the SWEDEN[15] self-consistent field and transformation programs. The open-shell calculations were performed with the ACESII[16] program system.

RESULTS AND DISCUSSION

Two approaches have been used to determine the HNO atomization energy (which can then be used to determine the heat of formation using the H, N, and O experimental[6] heats of formation). The first involves the three parameter correction formula proposed by Martin.[17] The strategy is to compute the atomization energy of the molecule of interest using the CCSD(T) correlation method and then to correct the computed value using the parameters and formula proposed by Martin. This formula depends on the number of σ and π bonds as well as the number of valence lone pair electrons in the molecule. For HNO, these constants are $n_\sigma=2$, $n_\pi=1$, $n_{\text{pair}}=3$. The adjustable parameters vary depending on the one-particle basis set, thus generally making the correction larger for smaller, less complete basis sets. We have used this approach in conjunction with the cc-pVTZ and cc-pVQZ basis sets—equilibrium geometries were taken from Ref. 5. With the cc-pVTZ basis the computed atomization energy is 194.7 kcal/mol and the corrected value is 205.5 kcal/mol, while the respective values for the cc-pVQZ basis set are 200.9 and 205.2 kcal/mol. Thus there is excellent agreement between the two corrected values with a difference of only 0.3 kcal/mol. Using the cc-pVQZ result as the best estimate for this approach, a heat of formation of HNO at 0 K of 26.5 kcal/mol is obtained (the HNO zero-point energy was taken from Ref. 5).

The second approach relies on the empirical observation[18] that many molecular properties converge in an exponential fashion when using a series of the correlation

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consistent[10] one-particle basis sets. In this vein, we have again examined the atomization energy of HNO using the CCSD (T) method in conjunction with the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets described earlier. The CCSD(T)/cc-pVQZ optimized structure[5] of HNO was used for all of these calculations. Fitting these data to the following formula

$$EAt = EAt_\infty + a*\exp(-b*n), \tag{1}$$

yields an EAt_∞ value (i.e., the atomization energy at the infinite basis set limit) of 204.3 kcal/mol. This value, however, is not directly comparable to the atomization energy from the first approach since Martin's semiempirical scheme accounts for small effects such as correlating the nitrogen and oxygen core electrons and the fact that the atoms are in the ground spin–orbit state. When computing the HNO heat of formation, the spin-orbit splitting of the atoms may be taken into account (for this second approach only) by using "nonrelativistic" (or spin–orbit averaged) atomic heats of formation. This is easily done with knowledge of the spin–orbit splittings[6] and using $\Sigma_j(2j+1)E_j/\Sigma_j(2j+1)$ to compute the "average" state. The effect of core correlation on the N–O bond energy is more problematic, however. Bauschlicher, Partridge, and Pradhan[19,20] have shown that core correlation increases the N–N bond energy by 0.8 kcal/mol and the C–N dissociation energy by 1.18 kcal/mol. In agreement, Martin[12] has recently found that core correlation increases the atomization energy of N_2 by 0.85 kcal/mol. It is expected that this effect on the N–O bond will be smaller than for N_2, but how much smaller is difficult to assess. Therefore we performed CCSD(T) calculations on N, O, and NO and have determined that core correlation increases the NO dissociation energy by 0.48 kcal/mol. Martin[12] has also shown that the atomization energy of NH_3 is increased by 0.67 kcal/mol. Thus taking one third of the effect for NH_3 and adding 0.48 kcal/mol for the NO bond yields a nonrelativistic atomization energy of HNO of 205.0 kcal/mol. Computing the HNO heat of formation from this gives 26.9 kcal/mol (0 K), which is in excellent agreement with the value from the first approach.

Averaging the values from the two approaches yields 26.7 kcal/mol. Estimating an uncertainty in this value is somewhat difficult. In Martin's[17] study, the corrected CCSD(T)/cc-pVQZ results gave a maximum error of only 0.98 kcal/mol and a mean absolute error of only 0.46 kcal/mol for the set of test molecules. There is no such statistical data available for use with Woon's[18] extrapolation technique. Nevertheless, given the excellent agreement between the two approaches and the very small residual errors found in Martin's[17] study, a conservative uncertainty would be twice the difference, ±0.8 kcal/mol. Thus our best computed $\Delta H^o_{f,0}$ value, 26.7±0.8 kcal/mol, shows that the currently accepted experimental value,[6] 24.5 kcal/mol, is in error. For completeness, our best estimate for $\Delta H^o_{f,298}$ is 26.0±0.8 kcal/mol. The H–NO bond energy is found to be 47.7 kcal/mol (298 K) using the new heat of formation of HNO, indicating that this bond is even weaker than previously thought.

CONCLUSIONS

A very accurate value for the heat of formation of HNO is determined using the CCSD(T) method in conjunction with large *spdf* and *spdfg* one-particle basis sets. Two different approaches have been used to assure the reliability of the computed value. Our best estimate for $\Delta H^o_{f,0}(\Delta H^o_{f,298})$ is 26.7±0.8 kcal/mol (26.0±0.8 kcal/mol), which indicates that the currently accepted experimental value,[6] 24.5 kcal/mol, is in error by roughly 2 kcal/mol.

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[16] ACESII is a computational chemistry package especially designed for coupled-cluster and many-body perturbation calculations. The SCF, transformation, correlation energy, and gradient codes were written by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett. The two-electron integrals are taken from the vectorized MOLECULE code of J. Almlöf and P. R. Taylor, and the derivative integrals are taken from the ABACUS program written by T. Helgaker, H. J. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor. The geometry optimization and vibrational analysis packages were written by J. F. Stanton and D. Bernholdt.

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