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On the H_2NO ($^2B_1$) → H_2 ($^1\Sigma_g$) + NO ($^2\Pi$) Mechanism. A Combined Density Functional Theory and *Ab Initio* Study

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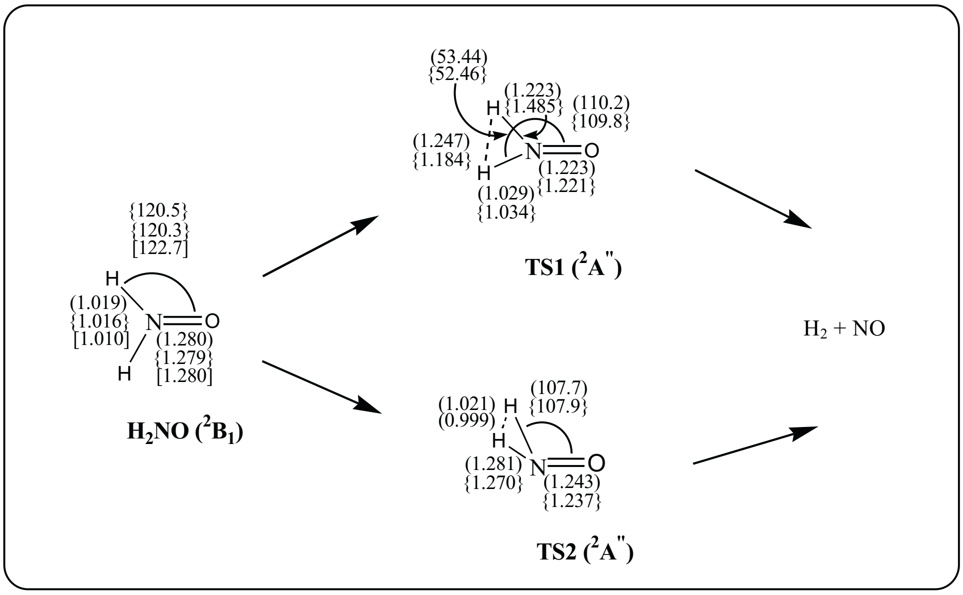
Nitrogen and oxygen containing species undergo chemical transformations that have recently attracted much attention in relation to important processes in fuel combustion [1,2]. Many previous theoretical studies have investigated the doublet potential energy surface of H_2NO [3–9]. However, the exact process by which H_2NO ($^2B_1$) decomposes into H_2 ($^1\Sigma_g$) + NO ($^2\Pi$) has been only briefly surveyed [3,5] by high level *ab initio* treatments.

The Gaussian-2 (G2) theoretical method has been applied by Yang *et al.* [5] to characterize the transition state, however, in their study the possibility of only one transition state was examined. This can lead to serious problems in the correct theoretical understanding of the transition state behavior for this mechanism. We have employed the GAUSSIAN 98 [10] set of codes to perform the B3LYP [11] density functional theory calculations, Gaussian-2 (G2) calculations [12], the quadratic complete basis set (CBS-Q) calculations with implemented B3LYP/CBSB7 geometry optimizations and frequency calculations (denoted CBS-QB3) [13], as well as the Gaussian-3 (G3) method with implemented B3LYP/6-31G(d) geometry optimizations and frequency calculations (denoted as G3B3) [14]. These popular methods have been evaluated in their examination of small molecular systems [see 15–17 and references therein].

The optimized geometry of all the molecules examined in this paper is shown in the figure-accompanying Table 1. The ( ) symbol is used to denote the B3LYP/6-31G(d) theoretical values, the { } symbol is for the B3LYP/CBSB7 data and the [ ] is for the experimental values. There exist two electronic states for H_2NO (the $^2A''$ state and the $^2B_1$ state). However, the $^2B_1$ state is by far more stable and is the compound experimentally observed so we shall only consider this electronic state. The MP2/6-31G(d) values from previous studies [5] predict that the planar H_2NO structure has an N–O bond length of 1.27 Å, an N–H bond length of 1.017 Å and a HNO bond angle of 120.3 degrees. These correlate quite well with empirically derived values.

Table 1. Harmonic vibrational frequencies calculated for the above shown geometries. The calculated parameters for both the geometry and frequencies are performed at the B3LYP/6-31G(d) (the ( ) symbol signifies this method for calculation and optimizations), and the B3LYP/CBSB7 method (the { } symbol signifies this method for calculation and optimizations) and [ ] signifies experimental data where available [4]; values outside of the parentheses in the table are calculated at the MP2(full)/cc-pVTZ level [3]. Frequencies are presented in units of cm^{-1}.



Molecule	Sym	Frequency					
$H_2NO(^2B_1)$	C_s	(395) (b_1) {215} 255	(1266) (b_2) {1271} 1286	(1408) (a_1) {1386} 1527	(1694) (a_1) {1682} 1706	(3417) (a_1) {3418} 3516	(3536) (b_2) {3543} 3658
$TS1(^2A'')$	C_s	(2037i) (a') {2042i} 2097i	(1427i) (a'') {1394i} 1450i	(733) (a') {749} 819	(1260) (a'') {1397} 1536	(1601) (a') {1653} 3090	(3361) (a') {3336} 3290
$TS2(^2A'')$	C_s	(1861i) (a') {1784i} 2017i	(586) (a'') {711} 958	(1145) (a') {1132} 1166	(1163) (a') {1161} 1177	(1448) (a') {1447} 1606	(2164) (a') {2310} 2442

The transition state (TS2) geometry with the MP2 method seems to correlate well with DFT providing for NO, HN, and HH bond lengths of 1.24, 1.27, and 0.98 Å respectively, as well as HNO bond angle of 107.4 degrees. Although, there is good agreement between the geometries predicted by the two methods, the calculated frequencies differ by around 40–100 cm^{-1}.

What is interesting to notice is that two imaginary frequencies are associated with TS1 (planar state the HHNO dihedral angle is 180.0 degrees when zero-point effects are included), thus providing evidence for its increasing instability, and probable non-existence throughout the course of the reaction path. However, TS2 only possesses one imaginary frequency that is indicative of transition states.

From Table 2 we present all the energies of the molecules shown in the figure associated with Table 1. It was not possible for us to obtain energies for TS1 using conventional *ab initio* approximations (*i.e.* CBS-Q, G1, G2MP2, G2, G3) due to Hartree-Fock (HF) convergence problems (HF is the preliminary optimization method for any of the methods described above). However, when the hybrid DFT method (B3LYP) is used for the optimization, we were able to obtain full convergence in agreement with previous theoretical investigations [3–9,18].

Table 2 shows the energy of reaction (ΔE_I). The variation from method to method can be also noticed. It is fairly obvious that DFT (B3LYP method) predicts a higher energy of reaction than any of the other theoretical algorithms employed. When a smaller basis set is used (B3LYP/6-31G(d) or B3LYP/B1 as shown in Table 2), we observe that the (0 K) energy of reaction is around 4 kilocalories per mole. However, when a larger basis set is used (in this case the CBSB7 (B2) basis set), the energy increases to 7.70 kcal/mol. The CBS-QB3 and G3B3 methods both predict very similar values of around 4 and 4.5 kcal/mol (when the zero-point energy is included into the energy), respectively. Also, we can notice that when the G2Q model is used (geometrical optimization at the QCISD (T)/6-311G(d,p) method), the energies (plus ZPE correction or ZPEC) is almost identical to our G2 result (with MP2/6-31G(d) optimizations), with the difference only being 0.07 kcal/mol. The highly computationally demanding QCISD (T) calculation of the energy seems to provide a value of around 5, which is in excellent agreement with our CBS-QB3 and G3B3 results, with a substantial saving in computer time and resources.

CBS-QB3 and the B3LYP/CBSB7 computational methods predict values for the forward barrier of TS1 (ΔE_{II}) that are around 4 kcal/mo lower than the barriers predicted by the G3 and G3B3 methods. However, the forward barrier of TS2 (ΔE_{III}) is calculated to be very similar when any of the methods is used. The excess stability associated with twisting out of planarity is predicted to be around 24 to 28 kcal/mol. Although intrinsic reaction coordinate (IRC) calculations were performed on this system we obtained a planar geometry for the transition state that is stabilized by non-planarity. TS2 is the most likely transition state for this reaction as is confirmed from density functional theory and advanced DFT based Gaussian methods (*i.e.* CBS-Q, G2, G3, *etc*). The higher energy needed for the activation barrier is justified by the increase in stability associated with this transition state structure. This in turn can allow for a higher specificity for this mechanism, whereby a transition state of high vibrational instability (*i.e.* TS1) might decompose into an intermediate structure(s), contrary to what is predicted by our calculations [3,19].

Among the most significant conclusions of this work is the theoretical analysis of the structure for proposed transition state. In many different studies TS1 (from Table 1) [3–9] is believed to exist and has been proposed as a possible transition state structure. However, from our previous discussions of its vibrational instability associated with this transition state we can conclude that it is simply not a highly probable pathway for the decomposition of H_2NO, regardless of its energetically favorable barrier.

Table 2. Energy is in hartrees/particle (0 K), means the sum of zero-point and electronic energies. ΔE_I is the difference in energy between the products H_2 and NO and H_2NO. ΔE_{II} is the forward activation barrier for the reaction through TS1; ΔE_{III} is the forward activation barrier for the reaction through TS2, ΔE_{IV} is the difference in energy between TS1 and TS2. Relative energies are in kcalories per mole. B1 is the 6-31G(d) basis set and B2 is the CBSB7 basis set. The references corresponding to the data in the table are: a. geometry optimized at the B3LYP/CBSB7 level of theory geometry; b. optimized at the MP2/6-31G(d) method; c. geometry optimized at the QCISD (T) /6-311G(d,p) level; d. [5]; e. geometry optimized at the B3LYP/6-31G(d) level; f. ICCI/cc-pVTZ//CAS/cc-pVDZ + ZPE [6]; g. CCSD (T)/6-311++G (3df, 3pd)//CCSD (T)/6-311++G (d, p) [7]; h. CISD + Q/cc-pVTZ + sp//CISD/cc-pVDZ + ZPE [8]; i. SOCI {2,2,9}/DZP without ZPE [9]; j. PMP4 (SDTQ, full)/cc-pVTZ//MP2/cc-pVTZ + ZPE [3]; k. QCISD (T, full)/cc-pVTZ//MP2/cc-pVTZ + ZPE [3].

Method	E (H_2NO)	E (H_2)	E (NO)	E (TS1)	E (TS2)	ΔE_I	ΔE_{II}	ΔE_{III}	ΔE_{IV}
B3LYP/B1	–131.08245	–1.1754824	–129.88816	–130.93060	–130.97370	11.8	95.2	68.2	27.0
B3LYP/B1 (0 K)	–131.05666	–1.1653390	–129.88362	–130.91476	–130.95888	4.83	89.0	61.3	27.7
B3LYP/B2	–131.12971	–1.1795710	–129.92670	–130.98217	–131.02249	14.7	92.5	67.2	25.3
B3LYP/B2 (0 K)	–131.10396	–1.1695050	–129.92217	–130.96592	–131.00709	7.70	86.6	60.7	25.8
CBS-QB3[a]	–130.91832	–1.1637240	–129.74620	–130.77971	–130.81859	5.26	86.9	62.5	24.4
CBS-QB3 (0 K) [a]	–130.92118	–1.1660841	–129.74856	–130.78265	–130.82159	4.10	86.9	62.4	24.4
G1 [b]	–130.90432	–1.1626450	–129.73678		–130.80596	3.07		61.7	
G1 (0 K) [b]	–130.90718	–1.1650060	–129.73914		–130.80888	1.90		61.6	
G2MP2 [b]	–130.90354	–1.1640000	–129.73386		–130.80453	3.56		62.1	
G2MP2 (0 K) [b]	–130.90640	–1.1663580	–129.73622		–130.80744	2.40		62.0	
G2 [b]	–130.90788	–1.1639970	–129.73761		–130.80853	3.93		62.3	
G2 (0 K) [b]	–130.91074	–1.1663580	–129.73997		–130.81143	2.77		62.3	
G2Q[c,d]						2.70		61.7	
G3B3 [e]	–131.00806	–1.1651150	–129.83388	–130.86436	–130.90950	5.68	90.1	61.8	28.3
G3B3 (0 K) [e]	–131.01092	–1.1674760	–129.83625	–130.86732	–130.91257	4.51	90.0	61.7	28.4
ICCI[f]							87.8		
CCSD (T) [g]						7.00		62.1	
CISD [h]									
SOCI [i]									
PMP4 (SDTQ) [j]						2.10	90.0	63.4	26.6
QCISD (T) [k]						4.90	90.9	62.8	28.1

In addition, when the geometry and vibrational modes are analyzed and mapped, TS2 is the most physically reasonable transition state structure for this reaction pathway regardless of the more energetically demanding conditions necessary for its formation. On a more computational side, we conclude that the CBS-QB3 and the G3B3 methods are computationally inexpensive methods for studying processes involving nitrogen and oxygen containing compounds.

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