High Level ab Initio and Density Functional Study of the CH + NO Reaction Product Branching

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Received: November 11, 1998; In Final Form: January 25, 1999

The thorough complete basis set, Gaussian ab initio, hybrid, and gradient-corrected density functional methods of computational studies were performed on the CH + NO reaction with the target being to determine the stable adduct intermediates, their enthalpies of formation, and the enthalpies for various branching pathways. This reaction has enormous importance in both combustion and atmospheric chemistry, and it is very important to have its accurate energy profile. The computed values are compared with the experimental values, and in almost all cases, the currently used energies should be corrected. Considering the accuracy of these high level ab initio methods, it is believed that the listed values in this paper are the most accurate up to date. The complete basis set computed values are the most accurate and are, for the enthalpy of formation at 0 K for HNCO and NCO, 39.2 and 28.3 kcal/mol, respectively. The H−N and N−C bond dissociation energies for HNCO are 109.6 and 87.4 kcal/mol. The suggested CBSQ enthalpies at 298 K for the CH + NO branching reaction are −3.47 eV for H (^2S) + NCO ($X^2\Pi$, $\tilde{A}^2\Sigma^+$), −4.42 eV CO ($X^1\Sigma^+$) + NH ($X^3\Sigma^-$); −3.03 eV O (^3P,^1D) + HCN ($X^1\Sigma^+$), −1.97 eV OH ($X^2\Pi$) + CN ($X^2\Sigma^+$, $A^2\Pi_i$), −1.69 eV N (^4S) + HCO (X^2A', $\tilde{A}^2A''$), −0.76 eV H (^2S) + CNO ($X^2\Pi$), and −1.01 eV H (^2S) + N (^2S) + CO ($X^1\Sigma^+$).

Introduction

Computational methods are becoming more and more reliable for the estimation of the energetic profile for relatively small molecular systems. Therefore, the computational methods are becoming an integrated part of the experimentalists research in fields where experimental data is hard to get if there are no qualitative estimations of the reaction's thermodynamic profile. This is certainly the case for the research in combustion and atmospheric chemistry. One reaction that attracts the attention of researchers in both of these fields is the CH + NO reaction.[1] The reaction is believed to be one of the main stream reactions in the nitric oxide reburning processes.[2] It is well established that this reaction occurs without barriers, and it has also been determined that the reaction is present in interstellar chemistry.[3] Considering its importance in so many different research fields, it does not come as a surprise that many theoretical[4] and experimental[5] studies were performed using a variety of techniques. It is interesting to point out that the rate constant of the reaction is not temperature sensitive, and at room temperature the rate constant is around 1.9×10^{-10}cm^3 mol^{-1} s^{-1}. Although the rate of the reaction seems to be determined accurately, little has been done by means of determining the product branchings that are so crucial for the proper modeling in both combustion and interstellar chemical processes that involve this reaction. One of the problems is that the thermodynamic values for various branching reactions, although available, have not been accurately determined. At this point, accurate theoretical values are needed. We have demonstrated in much of our research that both the complete basis set[6] and some density functional theory methods[7] are capable of accurately evaluating the thermochemistry for various chemical systems. Here we are presenting our computational data of the title reaction in comparison to the best experimental estimations currently available.

Computational Methods

All computational studies were performed with computational methods as they are implemented in the Gaussian 94[8] computational package. Several highly accurate ab initio approaches were used to compute accurate thermodynamic values. All of them are based on the knowledge that medium level ab initio methods, such as MP2[9] with a relatively small basis set, can generate acceptable geometries but not energies. The energies are evaluated with a high level of correctional ab initio methods. In this way, accurate thermodynamic properties of chemical systems can be evaluated. Three Gaussian ab initio approaches: G1,[10] G2,[11] and G2MP2,[12] as well as Petersson's complete basis set (CBSQ),[13] used in this paper belong to those computational approaches. From numerous currently available density functional theories, the two highly regarded BLYP[14,15] as gradient corrected and B3LYP[15,16] as hybrid density functional theory methods have been selected. A medium size 6-311G(2d,2p)[17] basis set was also used.[18]

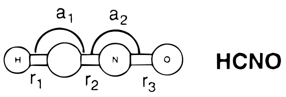
The energy computed in this paper is for the lower lying triplet or singlet of the products.

Results and Discussion

It is reasonable to assume that an encounter between the CH radical and the NO radical will result in the formation of a carbene-like HCNO molecule. Considering a classic Lewis structure, the HCNO as a singlet has one occupied orbital and one empty orbital. Therefore, this molecule can behave as an electron donor as well as an electron acceptor. The computed structural properties of the singlet HCNO are presented in Table 1. It is interesting to point out that, with the HF/6-31G(d)[19] ab initio theory model, which by definition does not include electron correlation, the structure was neither possible to obtain nor possible to optimize. Both MP2 and DFT methods generate linear structures that are very similar to each other, with an

10.1021/jp984394g CCC: $18.00 © 1999 American Chemical Society
Published on Web 03/06/1999

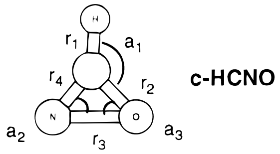
TABLE 1: Structural Properties of HCNO Computed with MP2 ab Initio and B3LYP and BLYP Density Functional Methods[a]



theory	r_1/Å	r_2/Å	r_3/Å	a_1/ (deg)	a_2/ (deg)
MP2/6-31G(d)	1.063	1.186	1.209	180.0	180.0
MP2/6-31G(d′)	1.066	1.186	1.209	180.0	180.0
B3LYP/6-311G(2d,2p)	1.059	1.157	1.200	180.0	180.0
BLYP/6-311G(2d,2p)	1.064	1.171	1.214	180.0	180.0
CCSD(T)/TZ2P	1.062	1.165	1.211	180.0	180.0

[a] r = bond distance. a = bond angle.

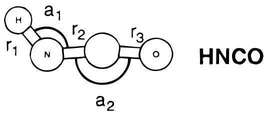
TABLE 2: Structural Properties of c-HCNO Computed with MP2 ab Initio and B3LYP and BLYP Density Functional Methods[a]



theory	r_1/Å	r_2/Å	r_3/Å	r_4/Å	a_1/ (deg)	a_2/ (deg)	a_3/ (deg)
MP2/6-31G(d)	1.082	1.343	1.728	1.255	132.5	46.2	50.6
MP2/6-31G(d′)	1.086	1.335	1.727	1.254	132.4	46.2	50.2
B3LYP/6-311G(2d,2p)	1.084	1.300	1.785	1.252	131.9	44.5	46.7
BLYP/6-311G(2d,2p)	1.091	1.314	1.838	1.269	130.9	43.6	45.6

[a] r = bond distance. a = bond angle.

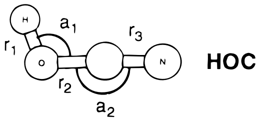
TABLE 3: Structural Properties of HNCO Computed with MP2 ab Initio and B3LYP and BLYP Density Functional Methods[a]



theory	r_1/Å	r_2/Å	r_3/Å	a_1/ (deg)	a_2/ (deg)
MP2/6-31G(d)	1.008	1.224	1.184	125.8	171.7
MP2/6-31G(d′)	1.008	1.228	1.178	124.5	171.4
B3LYP/6-311G(2d,2p)	1.005	1.211	1.164	124.4	172.8
BLYP/6-311G(2d,2p)	1.013	1.223	1.178	123.6	172.0
CCSD(T)/TZ2P	1.002	1.217	1.172	124.6	171.3

[a] r = bond distance. a = bond angle.

TABLE 4: Structural Properties of HOCN Computed with MP2 ab Initio and B3LYP and BLYP Density Functional Methods[a]



theory	r_1/Å	r_2/Å	r_3/Å	a_1/ (deg)	a_2/ (deg)
MP2/6-31G(d)	0.977	1.311	1.182	109.3	177.2
MP2/6-31G(d′)	0.970	1.308	1.183	109.5	177.3
B3LYP/6-311G(2d,2p)	0.966	1.299	1.153	110.4	176.4
BLYP/6-311G(2d,2p)	0.977	1.312	1.167	109.9	175.7

[a] r = bond distance. a = bond angle.

exception for the C−N bond distance (Table 1). From our experience with using the both ab initio and the density functional method, we believe that the most reliable structure is the one computed with the B3LYP/6-311G(2d,2p) theory model. If we considered that the coupled cluster ab initio calculation[21] is an extremely reliable method for the computation of the geometries of chemical systems, then the B3LYP hybrid DFT method is exceptionally reliable because the geometries differ less than 1% from each other (Table 1).

Because in the doublet CH one carbon orbital is occupied while one is empty, it can actually insert into nitrogen oxide. To explore this possibility we attempted to optimize the transition state structure for the CH addition to the NO. With both the ab initio and density functional theory methods, their attempt was not successful, and neither of the structures of the separated reactants or the "cyclic" isomers was obtained. Some of the obtained transition state structures were not reliable.[22] It is obvious that the transition state in energy is too close to the transition state structure, and for these cases it is very hard to optimize the transition state structures. The structure of the cyclic isomer (c-HCNO) is presented in Table 2. These structures have some very interesting properties. One of them is the exceptionally long N−O bond distance, which corresponds to the bond distance of the bond in formation or in breaking, which is a characteristic that can be observed in the transition states. Again, the structures computed with the gradient corrected BLYP/6-311G(2d,2p) theory is closer to the MP2/6-31G(d) computed structure than the hybrid B3LYP/6-31G(2d,2p) computed structure. In any case, the cyclic structure should be much less stable than the liner HCNO isomer.

As mentioned above, the HCNO as a first encounter compound in the CH and NO reaction should not be a very stable species. Again, by using very simple Lewis structures one can determine that the HNCO isomer should be the one that is the most stable. One way of transforming the HCNO isomer to HNCO is through cyclic c-HCNO isomers with the hydrogen rearrangement from carbon to nitrogen and the easy breaking of the already very long N−O bond. We had difficulty generating the transition state structures for those rearrangements. Because the structures are not properly optimized with both ab initio and density functional theory methods, it will not be reported here, but it is clear that the energy of the transition state is very close to the energy of the cyclic isomer. The structure of HNCO should be one of deep minimum, if not a global minimum, on the potential energy surface for the CH + NO reaction. It is very easy to obtain this structure at almost any theory level. Structural parameters for this molecule are presented in Table 3. Again we have a good agreement between the MP2 and gradient-corrected computed structure, but its is B3LYP/6-311G(2d,2p) that is close to the higher level of ab initio study (Table 3).

The same reasoning that was used for the production of the hydrogen isocyanate can be used for generating the hydrogen cyanate (HOCN) in the reaction of CH + NO. Hydrogen should be transferred from the carbon atom of the cyclic **c-HCNO** to oxygen with simultaneous N−O bond breaking. As in the case of the rearrangement in HNCO, the transition state structure for the HOCN formation was hard to optimize. Nevertheless, it is quite clear that in energy the transition state is very close to the energy of the cyclic isomer. The computed structural parameters for HOCN are presented in Table 4. It seems that the highest disagreement between the optimized structures is the CN multiple bond distance (r_3). The B3LYP/6-311G(2d,2p) computed bond distance is substantially shorter than the distances computed with both the MP2 and BLYP. Nevertheless, we believe that the geometry computed with the B3LYP hybrid

TABLE 5: Total Energies (hartrees) for HCNO, HNCO, and Cyclic HNCO and Their Relative Energies (eV) in Regard to the CH and NO[a]

theory	E(HCNO)	E(c-HNCO)	E(HNCO)	E(HOCN)	ΔH_{I}	ΔH_{II}	ΔH_{III}	ΔH_{IV}
G1 (0 K)	−168.346 973	−168.322 523	−168.455 961	−168.416 481	−5.32	0.67	−2.97	−1.89
G1	−168.342 613	−168.318 155	−168.451 732	−168.412 179	−5.38	0.67	−2.97	−1.89
G2 (0 K)	−168.347 415	−168.322 392	−168.456 773	−168.416 255	−5.30	0.68	−2.98	−1.87
G2	−168.343 055	−168.318 024	−168.452 544	−168.411 953	−5.36	0.68	−2.98	−1.87
G2MP2 (0 K)	−168.343 748	−168.318 116	−168.452 653	−168.411 665	−5.33	0.70	−2.96	−1.85
G2MP2	−168.339 388	−168.313 748	−168.448 424	−168.407 363	−5.39	0.70	−2.97	−1.85
CBSQ (0 K)	−168.355 952	−168.328 336	−168.464 634	−168.423 519	−5.34	0.75	−2.96	−1.84
CBSQ	−168.351 603	−168.323 953	−168.460 443	−168.419 253	−5.31	0.75	−2.96	−1.84
B3LYP (0 K)	−168.607 594	−168.570 977	−168.716 049	−168.671 064	−5.32	1.00	−2.95	−1.73
B3LYP	−168.626 756	−168.590 846	−168.737 432	−168.692 661	−5.55	0.98	−3.01	−1.79
BLYP (0 K)	−168.591 104	−168.555 948	−168.692 137	−168.645 733	−5.55	0.96	−2.75	−1.49
BLYP	−168.609 241	−168.575 169	−168.712 825	−168.666 417	−5.76	0.93	−2.82	−1.56

[a] (0 K) = sum of electronic and zero-point energies. The ab initio computed energies are 298 K and 1 atm. ΔH_{I} = relative energy of HCNO in regard to reactants CH and NO, ΔH_{II} = relative energy cyclic HCNO in regard to chain HCNO, ΔH_{III} = relative energy of HNCO in regard to HCNO, ΔH_{IV} = relative energy of HOCN in regard to HCNO.

TABLE 6: Computed Enthalpies of Formation (kcal/mol) for HCNO, HOCN, and HNCO Computed from Total Energies of These Compounds Ant Total Energies of Their Constitutional Elements[a]

theory	E(C)	E(H_2)	E(N_2)	E(O_2)	A	B	C
G1 (0 K)	−37.784 625	−1.165 006	−109.393 739	−150.147 889	38.7	−4.9	−29.7
G1	−37.782 265	−1.161 701	−109.390 434	−150.144 583	36.9	−6.8	−31.6
G2 (0 K)	−37.784 301	−1.166 358	−109.392 625	−150.148 211	38.4	−4.8	−30.2
G2	−37.781 940	−1.163 053	−109.389 321	−150.144 905	36.6	−6.7	−32.1
G2MP2 (0 K)	−37.783 887	−1.166 358	−109.389 484	−150.142 065	37.6	−5.1	−30.8
G2MP2	−37.781 527	−1.163 053	−109.386 179	−150.138 759	35.7	−7.0	−32.7
CBSQ (0 K)	−37.785 151	−1.166 085	−109.396 043	−150.162 752	39.2	−3.2	−29.0
CBSQ	−37.782 791	−1.162 781	−109.392 738	−150.159 446	37.3	−5.2	−31.0
B3LYP (0 K)	−37.856 166	−1.169 940	−109.554 338	−150.365 344	40.2	0.4	−27.8
B3LYP	−37.856 166	−1.180 013	−109.559 893	−150.369 073	34.3	−7.1	−35.2
BLYP (0 K)	−37.842 840	−1.159 707	−109.542 086	−150.362 917	34.4	0.1	−29.0
BLYP	−37.842 840	−1.169 601	−109.547 371	−150.366 327	28.9	−7.0	−36.1

[a] (0 K) = sum of electronic and zero-point energies. The ab initio computed energies are 298 K and 1 atm. Enthalpy of formation for HCNO isomers is computed as [2E(HCNO isomer) − 2E(C) − E(H_2) − E(N_2) − E(O_2)]627.5/2 + 169.9, $A = \Delta H_f$(HCNO), $B = \Delta H_f$(HOCN); $C = \Delta H_f$(HNCO).

density functional theory method should be the most reliable structure for HOCN.

Let us now partially explore the potential energy surface for these stationary points in regards to the reactants (CH + NO) and their first product HCNO. Total energies, as well as some of the reactants adducts and rearranged structures, are presented in Table 5. The formation of HCNO is predicted to be a very exothermic reaction. The enthalpy of the reaction computed with the CBSQ at 298 K is −5.31 eV. All Gaussian ab initio approaches basically produce the same energy change in formation of HCNO. As mentioned above, the hybrid DFT method is very accurate for computing thermodynamic properties, as the B3LYP/6-311G(2d,2p) energy differs only 0.02 eV from the CBSQ (0 K) energy (Table 5). As one would argue on the basis of the very unusual structure, the cyclic HCNO has higher energy. The predicted energy is around 0.75 eV. If the transition state structure for the HCNO rearrangement has a similar energy, it is not surprising that this structure has not yet been experimentally detected. It can very easily be transferred into HOCN or HNCO. The HOCO is predicted to be less stable in the gas phase with the enthalpy of the HCNO rearrangement to HOCN at −1.84 kcal/mol (Table 5). The B3LYP/6-311G(2d,2p) (0 K) enthalpy for this transformation is again in good agreement with the CBSQ estimated value. The most stable species on the potential energy surface is predicted to be HNCO. The exothermicity computed with the CBSQ for this rearrangement is −2.95 eV. Now the difference between the CBSQ (0 K) computed energy and the B3LYP/6-311G(2d,2p) energy is only 0.01 eV (Table 5). With the BLYP gradient-corrected DFT method, the computed energies are not in so close agreement with high level ab initio methods, as it is the case with the hybrid B3LYP density functional theory methods.

TABLE 7: Total Energies for Hydrogen and NCO Radical with H−NCO (D_1) Bond Dissociation Energy (kcal/mol) and the NCO (ΔH_f) Energy of Formation (kcal/mol)[a]

theory	E(H)	E(NCO)	D_1	ΔH_f	ΔH
G1 (0 K)	−0.500 000	−167.782 185	109.0	27.6	−3.56
G1	−0.497 639	−167.778 456	110.2	26.4	−3.57
G2 (0 K)	−0.500 000	−167.781 690	109.9	27.5	−3.51
G2	−0.497 639	−167.777 961	111.0	26.3	−3.53
G2MP2 (0 K)	−0.500 000	−167.777 126	110.1	27.2	−3.52
G2MP2	−0.497 639	−167.773 397	111.3	26.0	−3.53
CBSQ (0 K)	−0.499 818	−167.790 198	109.6	28.3	−3.55
CBSQ	−0.497 457	−167.786 504	110.7	27.1	−3.47
B3LYP (0 K)	−0.502 156	−168.043 784	106.7	27.0	−3.64
B3LYP	−0.502 156	−168.053 740	113.9	23.6	−3.62
BLYP (0 K)	−0.502 156	−168.027 775	101.8	24.0	−3.76
BLYP	−0.502 156	−168.037 277	108.8	20.8	−3.74

[a] (0 K) = sum of electronic and zero-point energies. The ab initio computed energies are 298 K and 1 atm. ΔH = enthalpy in eV for enthalpy (eV) for CH($X^2\Pi$) + NO($X^2\Pi$) → H(^2S) + NCO($X^2\Pi$, $\tilde{A}^2\Sigma^+$) reaction.

The enthalpy of formation was computed from the total energies of the HCNO isomers and the total energies of their building elements by including the experimental enthalpy of vaporization for graphite (169.9 kcal/mol). Thus, the obtained enthalpies of formation are listed in Table 6. In some of our previous studies we have demonstrated that this approach is highly reliable for computing the enthalpies of formation.[23] The most reliable of all applied computational methods is CBSQ.

TABLE 8: Enthalpy (eV) for $CH(X^2\Pi) + NO(X^2\Pi) \rightarrow CO(X^1\Sigma^+) + NH(X^3\Sigma^-)$ Reaction and the N−C (D_2) Bond Dissociation Energy (kcal/mol) for HNCO[a]

method	E(CH)	E(NO)	E(CO)	E(NH)	ΔH	D_2
G1 (0 K)	−38.412 212	−129.739 136	−113.177 224	−55.140 771	−4.53	86.6
G1	−38.408 907	−129.735 831	−113.173 919	−55.137 466	−4.53	88.1
G2 (0 K)	−38.412 590	−129.739 969	−113.177 498	−55.142 169	−4.55	86.0
G2	−38.409 285	−129.736 663	−113.174 193	−55.138 865	−4.55	87.5
G2MP2 (0 K)	−38.411 698	−129.736 221	−113.175 410	−55.140 026	−4.56	86.1
G2MP2	−38.408 393	−129.732 916	−113.172 105	−55.136 721	−4.56	87.6
CBSQ (0 K)	−38.412 132	−129.747 508	−113.181 486	−55.143 863	−4.51	87.4
CBSQ	−38.408 828	−129.747 508	−113.178 181	−55.140 559	−4.42	88.9
B3LYP (0 K)	−38.487 018	−129.925 023	−113.344 479	−55.231 355	−4.46	88.0
B3LYP	−38.493 439	−129.929 501	−113.349 531	−55.238 775	−4.50	93.6
BLYP (0 K)	−38.469 561	−129.917 619	−113.331 150	−55.214 130	−4.30	92.2
BLYP	−38.475 739	−129.921 803	−113.335 978	−55.221 249	−4.35	97.6
exptl est.					−4.62	

[a] (0 K) = sum of electronic and zero-point energies. The ab initio computed energies are 298 K and 1 atm.

TABLE 9: Enthalpy (eV) for $CH(X^2\Pi) + NO(X^2\Pi) \rightarrow O(^3P,^1D) + HCN(X^1\Sigma^+)$[a]

method	E(O)	E(HCN)	ΔH
G1 (0 K)	−74.982 049	−93.285 470	−3.16
G1	−74.979 688	−93.282 006	−3.18
G2 (0 K)	−74.982 030	−93.284 893	−3.11
G2	−74.979 669	−93.281 429	−3.13
G2MP2 (0 K)	−74.978 678	−93.282 494	−3.08
G2MP2	−74.976 317	−93.279 030	−3.10
CBSQ (0 K)	−74.987 068	−93.286 262	−3.09
CBSQ	−74.984 707	−93.282 804	−3.03
B3LYP (0 K)	−75.085 571	−93.438 014	−3.04
B3LYP	−75.085 571	−93.454 310	−3.18
BLYP (0 K)	−75.073 567	−93.417 376	−2.82
BLYP	−75.073 567	−93.433 107	−2.97
exptl est			−3.17

[a] (0 K) = sum of electronic and zero-point energies. The ab initio computed energies are 298 K and 1 atm.

TABLE 10: Enthalpy (eV) for $CH(X^2\Pi) + NO(X^2\Pi) \rightarrow OH(X^2\Pi) + CN(X^2\Sigma^+, A^2\Pi_i)$[a]

method	E(OH)	E(CN)	ΔH
G1 (0 K)	−75.642 142	−92.583 364	−2.02
G1	−75.638 837	−92.580 058	−2.02
G2 (0 K)	−75.643 908	−92.582 759	−2.02
G2	−75.640 603	−92.579 453	−2.02
G2MP2 (0 K)	−75.640 924	−92.580 354	−2.00
G2MP2	−75.637 619	−92.577 047	−2.00
CBSQ (0 K)	−75.648 937	−92.586 333	−2.06
CBSQ	−75.645 632	−92.583 027	−1.97
B3LYP (0 K)	−75.748 418	−92.734 209	−1.92
B3LYP	−75.756 862	−92.739 114	−1.99
BLYP (0 K)	−75.734 254	−92.725 662	−1.98
BLYP	−75.742 350	−92.730 381	−2.05
exptl est			−2.19

[a] (0 K) = sum of electronic and zero-point energies. The ab initio computed energies are 298 K and 1 atm.

There are some experimental values for HCNO and HNCO.[24] The ΔH_f(HCNO) is 52 kcal/mol and ΔH_f(HNCO) −25 ± 3 kcal/mol. A recent experimental study by Reisler and co-workers suggested a value of −27.8 ± 0.4 kcal/mol as the enthalpy of formation for HNCO.[25] Our B3LYP/6-311G(2d,2p) with zero-point energy correction perfectly agrees with this value (Table 6). In fact, our computed value is −27.8 kcal/mol. Usually more accurate, the CBSQ (0 K) ab initio method is −29.0 kcal/mol, which is slightly higher than the Reisler value. The enthalpy of formation for HCNO is quite different than the suggested value. The CBSQ value is 39.2 kcal/mol, which is in quite good agreement with the 40.2 kcal/mol obtained with the B3LYP/6-311G(2d,2p) (0 K), but not with the 52 kcal/mol suggested previously.[24] The suggested enthalpy of formation for HOCN at 0 K is −3.2 kcal/mol (Table 6).

Let us now evaluate the H−NCO bond dissociation energy and the heat of formation for NCO. Both of these values are available experimentally, therefore it will be very interesting to determine our computational values with those obtained experimentally. The computed values are presented in Table 7. The most recent experimental determination of the threshold for the NH fission comes from the UV photoexcitation experiment by Brown and co-workers.[26] It was estimated that the bond dissociation energy is 109.7 kcal/mol (260.6 nm). This value is in relatively good agreement with some recent computational studies.[27] Our CBSQ (0 K) value differs from the suggested value by only 0.1 kcal/mol. The hybrid B3LYP/6-311G(2d,2p) computed bond dissociation energy is slightly lower than the CBSQ value (106.7 kcal/mol), which we have observed for some other chemical systems previously.[28] On the other hand, the gradient-corrected values are closer to the experimental value, as it is also in the case of the H−NCO bond dissociation energy (Table 7). The estimated enthalpy of formation of NCO is estimated to be 30.3 ± 0.3 kcal/mol.[25] According to our results, this value is slightly lower. The CBSQ (0 K) computed enthalpy of formation is 28.3 kcal/mol, while the B3LYP/6-311G(2d,2p) (0 K) is even slightly lower and agrees well with the G2MP2 (0 K) enthalpy of formation of the CNO radical. We are suggesting 28.3 kcal/mol as a more accurate enthalpy of formation for the NCO radical. The generally used enthalpy for the CH + NO → H + NCO reaction is −3.22 eV at 0 K.[1] It is very important to know the accurate value for the exothermicity of this reaction because together with the exothermicity values for other possible reactions, it will determine the branching pattern for the CH + NO reaction. Our suggestion is that the exothermicity for this reaction is −3.47 eV at 298 K, as computed by CBSQ (Table 7). The zero-point corrected value should be −3.55 eV, which is relatively close to the −3.64 eV computed with the B3LYP/6-311G(2d,2p) (Table 7).

It is very important to have accurate values for the CH + NO branching reaction because these values will determine the ratio of the branching products. First we will explore a major branching channel for the CH + NO reaction, the formation of CO + NH.[29] Total energy and exothermicity for this reaction with the N−C bond dissociation for the most stable HNCO isomer from which the decomposition products are formed are presented. In the literature, there are many values suggested as the C−N bond dissociation energy for HNCO, starting from 80−120 kcal/mol. Our high level of ab initio study suggests a value of 87.4 kcal/mol. It is interesting to point out that for polar bonds, such as peroxides and C−O, the hybrid density

TABLE 11: Enthalpies (eV) for Three CH($X^2\Pi$) + NO($X^2\Pi$) Branching Reactions[a]

method	E(N)	E(HCO)	E(CNO)	ΔH_{I}	ΔH_{II}	ΔH_{III}
G1 (0 K)	−54.517 736	−113.697 471	−167.681 286	−1.74	−0.81	−1.19
G1	−54.515 376	−113.693 671	−167.677 151	−1.75	−0.82	−1.15
G2 (0 K)	−54.517 960	−113.698 846	−167.681 388	−1.75	−0.78	−1.17
G2	−54.515 599	−113.695 045	−167.677 253	−1.76	−0.79	−1.13
G2MP2 (0 K)	−54.516 306	−113.695 974	−167.677 147	−1.75	−0.80	−1.19
G2MP2	−54.513 945	−113.692 173	−167.673 012	−1.76	−0.80	−1.15
CBSQ (0 K)	−54.520 256	−113.704 205	−167.690 887	−1.76	−0.85	−1.14
CBSQ	−54.517 896	−113.700 407	−167.686 793	−1.69	−0.76	−1.01
B3LYP (0 K)	−54.598 543	−113.877 198	−167.945 043	−1.73	−0.96	−0.90
B3LYP	−54.598 543	−113.890 125	−167.953 764	−1.79	−0.90	−0.74
BLYP (0 K)	−54.583 405	−113.859 817	−167.932 416	−1.52	−1.16	−0.68
BLYP	−54.583 405	−113.872 184	−167.940 529	−1.58	−1.10	−0.53
exptl est				−1.80	−0.61	−1.12

[a] (0 K) = sum of electronic and zero-point energies. The ab initio computed energies are 298 K and 1 atm. ΔH_{I} = enthalpy for formation of N(^{4}S) + HCO(X^2A', $\tilde{A}^2A''$), ΔH_{II} = enthalpy for formation of H(^{2}S) + CNO($X^2\Pi$), ΔH_{III} = enthalpy for formation of H(^{2}S) + N(^{2}S) + CO($X^1\Sigma^+$).

functional method computes bond dissociation energies that are very close to the experimental or high level ab initio values.[30] This is also true for the C−N bond dissociation energy for HNCO. The CBSQ (0 K) computed energy is 87.4 kcal/mol, while the B3LYP/6-311G(2d,2p) (0 K) computed energy is 88.0 kcal/mol (Table 8). There is an extraordinary agreement between the high level of ab initio study and hybrid DFT evaluated energies. The generally used exothermicity for the reaction presented in Table 8 is -4.62 eV at 298 K.[1] Our best evaluation with the CBSQ at 298 K is −4.42 eV, with a difference 0.2 eV that can be crucial for the correct evaluation of the branching pattern for the CH + NO reaction. At 0 K this value is 4.51 eV, which is in relatively good agreement with the −4.46 eV computed with the B3LYP/6-311G(2d,2p) (0 K) hybrid DFT method (Table 8).

As we have demonstrated on the example of exothermicity for the CH + NO reaction with the formation of H + NCO and NH + CO as products, the used values in the literature substantially (∼0.2 eV) disagree with both ab initio and density functional theory values. Now we would like to perform a systematic study of the exothermicity of some other branching reactions. One of them is the formation of O and HCN (Table 9). The previously used value is −3.17 eV.[1] As in the previous case, we find it necessary to correct this value; however, the correction should be in the opposite direction. Our predicted value is −3.03 eV, as computed with the CBSQ ab initio approach at 0 K (Table 9). The suggested value is −3.09 eV. Again, our B3LYP/6-311G(2d,2p) computed value at 0 K is in perfect agreement with the CBSQ values. It is estimated that the enthalpy of the reaction is −3.04 eV (Table 9). Another possibility is that in this reaction, HNC is actually formed instead of HCN. This reaction is highly unlikely because the activation barrier for the HNC rearrangement into HCN is relatively low.[31]

One of the other branching possibilities for the title reaction is the formation of the OH and the CN radicals. The currently used enthalpy for this reaction is −2.19 eV. Again, we have found a problem with this reaction, in that it is 0.22 eV too negative. Our suggestion is −1.97 eV at 298 K and −2.06 at 0 K (Table 10). The hybrid density functional theory method computes an enthalpy of the reaction which deviates even more from the currently used values (Table 10).

Finally, we would like to evaluate the enthalpy of three more branching reactions. First, we will explore the branching reaction in which N + HCO is formed, second we will explore the reaction in which H + CNO is formed, and third, we will explore the reaction in which H + N + CO is formed (Table 11). Again we have a discrepancy between the currently used enthalpies for these three reactions. They differ by approximately ±0.15 eV. This is a very high disagreement if the ratio of product is to be computed from these values. The CBSQ values presented in Table 11 are the ones that are suggested by us as the most accurate values. Hybrid DFT generated values with zero-point correction are relatively close to the CBSQ (0 K) energies.

Conclusion

Considering the fact that the complete basis set and Gaussian ab initio methods are very accurate ab initio approaches for exploring the potential energy surface for many chemical reactions, there is a certain confidence in that the computed energies presented in this paper are more accurate than the currently used values. In numerous papers of ours we have demonstrated that the hybrid DFT methods are exceptionally accurate when small polar chemical systems are explored, as it is the case in this paper. Further support that the computed values should be very accurate is the agreement between the CBSQ ab initio and the B3LYP hybrid DFT methods in the computed energies. It was definitively established that the most stable HC + NO adduct should be HNCO and that the branching products can come from this, as well as from the HCNO and the HOCN isomers that are interconnected with the high energy cyclic isomer. The suggested enthalpy of formation at 0 K for HNCO and NCO are 39.2 and 28.3 kcal/mol, respectively. The H−N and N−C bond dissociation energies for HNCO are 109.6 and 87.4 kcal/mol. The enthalpies of HC + NO branching reaction are −3.47 eV for H(^{2}S) + NCO($X^2\Pi$, $\tilde{A}^2\Sigma^+$), −4.42 eV CO($X^1\Sigma^+$) + NH($X^3\Sigma^-$); −3.03 eV O(^{3}P,^{1}D) + HCN($X^1\Sigma^+$), −1.97 eV OH($X^2\Pi$) + CN($X^2\Sigma^+$, $A^2\Pi_i$), −1.69 eV N(^{4}S) + HCO(X^2A', $\tilde{A}^2A''$), −0.76 eV H(^{2}S) + CNO($X^2\Pi$), and −1.01 eV H(^{2}S) + N(^{2}S) + CO($X^1\Sigma^+$).

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