J. Phys. Chem. A **1998,** *102,* 9255−9260

Complete Basis Set ab Initio Study of the CH Insertion Reaction with Water, Ammonia, and Hydrogen Fluoride

Branko S. Jursic

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Received: March 23, 1998; In Final Form: June 8, 1998

The mechanisms of the doublet CH radical reaction with ammonia, water, and hydrogen peroxide were computationally studied with complete basis set ab initio methods. Several different reaction pathways are considered, including hydrogen transfer, fusing of radicals, and the CH radical insertion reaction. It was demonstrated that the insertion reaction has the lowest activation barrier. Enthalpies of several reactions were explored, and it was demonstrated that complete basis set ab initio method is highly accurate for computing thermal properties of these chemical systems.

Introduction

There is considerable interest in the chemistry of such small molecular species as the CH radical. It is believed that this radical plays an important role in the growing field of combustion and atmospheric chemistry. It then does not come as a surprise that there are experimental studies of the CH radical with numerous small molecules.[1] Because of the importance of this reaction, many high levels of computational studies were performed on the interaction of such radicals with small polar chemical entities. There are several publications on the CH radical insertion reaction into hydrogen, ethylene, and methane.[2] Exactly the same insertion reaction was studied previously by Wang and co-workers at relatively modest theory levels (MP2/6-31G(d,p)).[3] We would like to present our complete basis set ab initio computational study of exploring potential energy surfaces for the CH radical insertion reaction with water, ammonia, and hydrogen fluoride.

Computational Methods

All computational studies were performed with the Gaussian 94[4] computational package with ab initio and density functional methods according to how they are implemented in the computational package. The complete basis set (CBS) method was developed by Petersson and co-workers.[5] The family name reflects the fundamental observation underlying these methods, namely, that the largest error in the ab initio calculations results from basis set truncation. The energy of the chemical system is computed from a series of calculations. Initial calculation starts with geometry optimization and frequency calculation at the HF/6-31G(d′) theory level.[6] The geometry is further optimized at the MP2/6-31G(d′)[7] theory level with single-point energy calculation at QCISD(T)/6-31+(d′),[7] MP4(SDQ)/CBSB4,[9] and MP2/CBSB3. The model also has empirical corrections for spin contamination and a size-consistent high-order correction. Explanation for basis set abbreviation can be found elsewhere.[10] All energies are computed on the fully optimized structures of radicals and neutral molecules. The reported geometries in this paper are computed with the MP2/6-31G(d′) theory model, and unless stated otherwise, the reported energies are computed at the CBSQ(0 K) theory level.

Results and Discussion

In many of our pervious computational studies, we have indicated that the complete basis set ab initio method is exceptionally accurate when thermodynamic properties such as bond dissociation energy,[11] complexation energy,[12] heat of formation,[13] heat of the reaction,[14] and activation barriers are computed.[14−16] Here, we are exploring the potential surface for the reaction of the CH radical with ammonia, water, and hydrogen fluoride. We believe that the computational studies outlined here are the most accurate studies of today.

The outer-shell carbon electron configuration is such that there is a nonbonding (lone) s-electron pair capable of forming hydrogen bonds with strong proton donors, such as hydrogen chloride. In addition, the CH radical might have a polar carbon−hydrogen bond that might act as proton donor and form a hydrogen-bonding complex with a strong base, such as ammonia. Therefore, one might expect that the first step in the CH radical reaction with ammonia, water, and hydrogen fluoride molecules is the formation of the reactants' hydrogen-bonding complexes. To explore this possibility, we have to perform the CBSQ ab initio study of those hydrogen-bonding complexes. Structures of hydrogen-bonding complexes with the CH radical as a proton donor and a proton acceptor are presented in Figure 1. The hydrogen-bonding distances are exceptionally long, indicating very small, if any, energy stabilization by the reactant complexation. For instance, in **HBC1**, the complex between CH radical as a proton donor and ammonia, the computed bond distance is 2.569 Å, very close to the H−O hydrogen bond distance in the **HBC2**. In the case of hydrogen fluoride as proton acceptor, we were not able to find any hydrogen-bonding complex. It is obvious that the hydrogen-bonding complex with the CH radical as a proton donor can be formed only in the case of very strong proton acceptors, such as ammonia.

The CH radical cation is not a good proton acceptor. The hydrogen-bonding complex with ammonia as a proton donor was not able to be optimized, and only complexes with water and hydrogen fluoride that have lower pK_a values were capable of forming the complexes. With stronger proton donors such as hydrogen fluoride, the hydrogen-bonding distance comes closer to 2 Å, which is what is generally observed as an average hydrogen-bonding distance, indicating that the highest stabiliza-

10.1021/jp981587v CCC: $15.00

TABLE 1: Total Energies (a.u.) of Components Involved in the CH Radical Insertion Reaction

theory level	E_{CH}	E_{NH_3}	E_{H_2O}	E_{HF}
HF/6-31G(d′)	−38.266 570	−56.183 764	−76.006 573	−99.996 684
HF/6-31G(d′)(0 K)	−38.259 627	−56.146 674	−75.983 522	−99.986 838
MP2/6-31G(d′)	−38.341 501	−56.353 153	−76.196 935	−100.194 052
QCISD(T)/6-31+G(d′)	−38.372 875	−56.379 952	−76.221 060	−100.220 391
MP4/CBSB4	−38.377 509	−56.409 033	−76.250 654	−100.239 380
MP2/CBSB3	−38.379 267	−56.448 254	−76.314 849	−100.324 499
CBS-Q(0 K)	−38.412 158	−56.459 103	−76.336 490	−100.359 172
CBS-Q	−38.408 853	−56.455 296	−76.332 711	−100.355 868

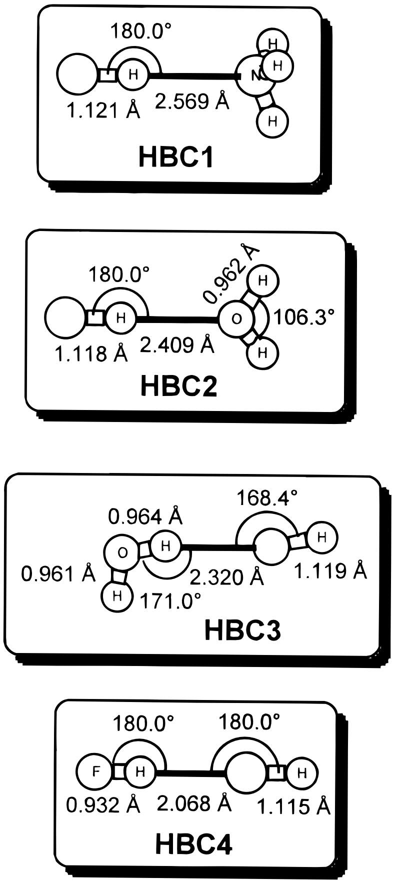

Figure 1. Hydrogen-bonding complexes with the CH radical as a hydrogen donor and a hydrogen acceptor.

tion can be obtained in the complex with hydrogen fluoride as a proton donor. To demonstrate this effect, we have computed total energies for all reactants (Table 1) and their hydrogen-bonding complexes (Table 2).

As was already indicated on the basis of the structural parameters, the hydrogen bondings are not very strong. The average hydrogen bond is around 5 kcal/mol. It was estimated that the hydrogen-bonding energy for C−H···NH_3 is only 1.0 kcal/mol, and it is very similar to the energy for the C−H···OH_2 hydrogen bond (Table 3). As was mentioned above, in the case of hydrogen fluoride as hydrogen acceptor, hydrogen bonding could not be obtained. On the other hand, hydrogen bonding with the CH radical as the hydrogen acceptor seems to be much stronger, and the complex with ammonia does not seem to form. The estimated complexation energy with water as the proton donor is 1.9 kcal/mol, and with hydrogen fluoride as the proton donor is 4.3 kcal/mol (Table 3). Both of these energies are not strong enough to suggest that this might be a major reaction pathway in the reaction with CH radical. Nevertheless, one can suggest that the path with CH as radical hydrogen acceptor is one that might be preferable. To further explore this possibility, we have optimized transition-state structures for proton transfers from ammonia and water (Figure 2). Due to a convergence problem, we were not able to optimize the transition-state structure for the proton transfer from hydrogen fluoride to the CH radical. Common to both of these structures is that they are very late in the potential energy surface and therefore have energy very close to the CH_2 triplet and NH_2 and OH radical as products of this proton transfer. The resulting carbene and radical can later recombine by forming H_2CNH_2 and H_2COH radicals, respectively. Such formed radicals can, after elimination of the hydrogen radical, produce stable H_2CNH and H_2CO molecules.

There is a considerable problem with transition-state structures presented in Figure 2. They are, in fact, much closer in geometry to the hydrogen-bonding complexes of triplet CH_2 as hydrogen donor with NH_2 and OH radical as hydrogen acceptor although at the HF theory level both of these transition-state structures have one imaginary frequency. Of course, that is not necessarily true for geometries generated at the MP2/6-31G(d′) theory levels. By separate calculations it was demonstrated that actual transition-state structures **HTTS1** and **HTTS2** have geometries very close to the corresponding hydrogen-bonding complexes. Therefore, the computed activation energy for this hydrogen transfer should be taken with caution.

Total energies and activation barriers computed for those two hydrogen-transfer reactions are presented in Table 4. It was estimated that the activation barrier for hydrogen transfer from ammonia to the CH radical is around 6.5 kcal/mol, while for the hydrogen transfer in a water molecule, this value is 18.5 kcal/mol (Table 4). It is interesting to point out that the computed activation barriers at HF/6-31G(d′) are negative, indicating the necessity of electron correlation interactions for the proper description of this very sensitive potential energy surface. Our attempt to generate transition-state structures for the reaction between triplet and triplet CH_2 carbene with the NH_2, OH, and the F radical failed. One can offer the explanation that the activation barrier is too low to allow computational study, therefore the reactants are combined without reaction barrier, and that the rate-determining state in this transformation is actually the hydrogen proton transfer from ammonia, water, and hydrogen fluoride to the CH radical. There is certainly no stronger evidence for this process than the results presented above.

Our attempt to locate transition-state structures for the addition of the CH radical to the ammonia, water, or hydrogen fluoride molecules failed. The same is true for a transition state of the addition of the triplet CH_2 carbene and NH_2, OH, and F radicals. One can argue that this reaction might occur without reaction barriers, and therefore it is not possible to locate them. The structures of the CH radical adducts computed at the MP2/6-31G(d′) theory level are presented in Figure 3. The C−heteroatom bond distances are unusually long, indicating that this reaction might not be performed after all. Total energies for the $HCNH_3$, $HCOH_2$, and the HCFH radical adducts and their

TABLE 2: Total Energies (au) for Hydrogen Complexes between CH Radical and Ammonia, Water, and Hydrogen Fluoride[a]

theory level	ΔE_{I}	ΔE_{II}	ΔE_{III}	ΔE_{IV}
HF/6-31G(d′)	−94.453 718	−114.279 661	−114.279 157	−138.274 284
HF/6-31G(d′)(0 K)	−94.407 911	−114.248 019	−114.246 451	−138.253 731
MP2/6-31G(d′)	−94.699 283	−114.539 180	−114.545 255	−138.547 045
QCISD(T)/6-31+G(d′)	−94.756 755	−114.597 846	−114.599 747	−138.603 824
MP4/CBSB4	−94.789 865	−114.625 735	−114.633 612	−138.627 019
MP2/CBSB3	−94.830 984	−114.692 620	−114.700 190	−138.715 366
CBS-Q(0 K)	−94.872 788	−114.751 008	−114.751 696	−138.778 259
CBS-Q	−94.865 538	−114.743 658	−114.745 089	−138.772 742

[a] E_{I} = total energy for the C−H···NH_3 complex; E_{II} = total energy for the C−H···OH_2 complex; E_{III} = total energy for the HO−H···CH complex; E_{IV} = total energy for the F−H···CH complex.

TABLE 3: Computed Hydrogen-Bonding Complexation Energies (kcal/mol) for Various CH Complexes[a]

theory level	ΔE_{I}	ΔE_{II}	ΔE_{III}	ΔE_{IV}
HF/6-31G(d′)	2.1	4.1	3.8	6.9
HF/6-31G(d′)(0 K)	1.0	3.1	2.1	4.6
MP2/6-31G(d′)	2.9	0.5	4.3	7.2
QCISD(T)/6-31+G(d′)	2.5	2.5	3.6	6.6
MP4/CBSB4	2.1	−1.5	3.4	6.4
MP2/CBSB3	2.2	−0.9	3.8	7.3
CBS-Q(0 K)	1.0	1.5	1.9	4.3
CBS-Q	0.9	1.3	2.2	5.0

[a] ΔE_{I} = the C−H···NH_3 complexation energy; ΔE_{II} = the C−H···OH_2 complexation energy; ΔE_{III} = the HO−H···CH complexation energy; ΔE_{IV} = the F−H···CH complexation energy.

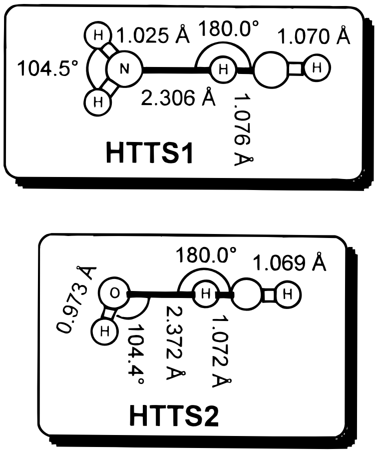

Figure 2. Transition-state structures for the CH radical abstraction of hydrogen from ammonia and water.

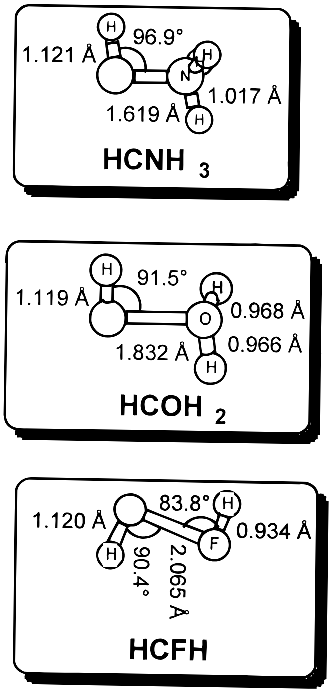

Figure 3. Structures of the CH radical adduct with ammonia, water, and hydrogen fluoride.

relative energies in regard to the CH radical and neutral molecules are presented in Table 5. The most stable adduct with the CH radical was formed with ammonia. The computed stabilization energy is 27.3 kcal/mol, while the stabilization energy for CH radical fusion with hydrogen fluoride is only 2.9 kcal/mol (Table 5). That definitely indicates that these fused compounds, if formed, are metastable and, probably through rearrangement, form a more stable product.

The structures of the triplet CH_2 carbene fused products with NH_2, OH, and F radicals are presented in Figure 4. All compounds are radicals in their doublet electronic configuration. Both H_2CNH_2 and H_2COH are actually hydrogen radicals bound to stable organic molecules, $H_2C{=}NH$ and $H_2C{=}O$. The bond distances, as well as bond angles, demonstrate that the carbon

TABLE 4: Total Energies (au) for Hydrogen Abstraction Reaction with CH Radical and Corresponding Activation Barriers (kcal/mol)[a]

theory level	E_{I}	E_{II}	ΔE_{I}	ΔE_{II}	ΔE_{III}
HF/6-31G(d′)	−94.468 483	−114.290 210	−11.4	−10.7	−6.9
HF/6-31G(d′)(0 K)	−94.429 896	−114.263 891	−14.8	−13.0	−10.9
MP2/6-31G(d′)	−94.687 867	−114.521 241	4.3	10.8	15.1
QCISD(T)/6-31+G(d′)	−94.741 278	−114.571 123	7.2	14.3	18.0
MP4/CBSB4	−94.771 696	−114.596 429	9.3	19.9	23.3
MP2/CBSB3	−94.811 251	−114.657 974	10.2	22.7	26.5
CBS-Q(0 K)	−94.860 935	−114.722 246	6.5	16.6	18.5
CBS-Q	−94.854 048	−114.715 717	6.3	16.2	18.4

[a] E_{I} = total energy for hydrogen transfer from ammonia to the CH radical; E_{II} = total energy for hydrogen transfer from water to the CH radical; ΔE_{I} = relative energy for transition-state structure for hydrogen transfer from ammonia to the CH radical in regard to the separate reactants; ΔE_{II} = relative energy for transition-state structure for hydrogen transfer from water to the CH radical in regard to the separate reactants; ΔE_{III} = relative energy for transition-state structure for hydrogen transfer from water to the CH radical in regard to the HON−H···CH complex.

TABLE 5: Total Energies (au) for the CH Radical Adducts and Their Relative Energies (kcal/mol) in Regard to Separated Reactants[a]

	E_I	E_{II}	E_{III}	ΔE_I	ΔE_{II}	ΔE_{III}
A	−94.477 267	−114.285 454	−138.269 251	−16.9	−7.7	−3.8
B	−94.424 618	−114.251 052	−138.251 152	−11.5	−5.0	−2.9
C	−94.747 100	−114.562 765	−138.546 635	−32.9	−15.3	−7.0
D	−94.801 155	−114.613 477	−138.597 946	−30.3	−12.3	−2.9
E	−94.829 440	−114.641 734	−138.618 498	−26.9	−8.5	−1.0
F	−94.882 874	−114.714 837	−138.708 472	−34.7	−13.0	−3.0
G	−94.914 736	−114.763 895	−138.775 771	−27.3	−9.6	−2.9
H	−94.909 863	−114.757 972	−138.770 044	−28.7	−10.3	−3.3

[a] A = HF/6-31G(d′); B = HF/6-31G(d′)(0 K); C = MP2/6-31G(d′); D = QCISD(T)/6-31+G(d′); E = MP4/CBSB4; F = MP2/CBSB3; G = CBS-Q(0 K); H = CBS-Q; E_I = total energy for $HCNH_3$; E_{II} = total energy for $HCOH_2$; E_{III} = total energy for HCFH; ΔE_I = enthalphy for the HC + NH_3 reaction; ΔE_{II} = enthalpy for the HC + OH_2 reaction; ΔE_{III} = enthalpy for the HC + FH reaction.

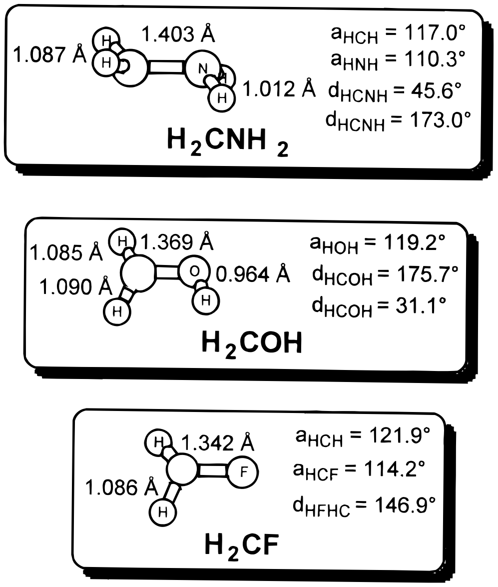

Figure 4. Structures of the CH_2 carbene fused compounds with NH_2, OH, and F radicals.

atom is sp^2-hybridized. One can argue that a complex between these molecules and a hydrogen radical is not a stable chemical system. If this is true, then the hydrogen radical complexed molecules are metastable, and their energy might be substantially higher than the energy of separated triplet CH_2 carbene and ammonia, water, and hydrogen fluoride. To confirm this assumption, total energies for the reactants and their products of fusion are computed (Tables 6 and 7). The energy difference between fused products and separate reactants are presented in Table 7. All three fusion reactions (CH_2 + NH_2, CH_2 + OH, and CH_2 + F) are extremely endothermic. All CBSQ estimated energies are above 100 kcal/mol (Table 7), indicating that these transformations are unlikely to occur.

Let us finally explore the direct CH radical insertion reaction into ammonia, water, and hydrogen fluoride. The MP2/6-31G-(d) computed geometries of corresponding transition-state structures are presented in Figure 5. All transition-state geometries are what would be expected for concerted carbon−hydrogen and carbon−heteroatom bond formation. For instance, the N−H bond distance in breaking is 1.156 Å, with the C−H bond in formation of 1.374 Å. It comes as a surprise that the C−N bond distance for the CH addition to ammonia is so advanced. It is actually almost fully formed. The C−O bond distance in **ITS2** is slightly longer still and therefore closer in structural properties to the reactant than in the case of **ITS1**. The loose transition structure is obtained for a reaction with hydrogen fluoride, suggesting that the activation barrier for this reaction might be very low. The total energies for the transition states and activation barriers for the insertion reactions are presented in Table 8. The CBSQ estimates that the CH radical

TABLE 6: Total Energies (au) for Triplet CH_2, and the Doublet NH_2, OH, and F Radicals[a]

	E_I	E_{II}	E_{III}	E_{IV}
A	−38.921 579	−55.556 663	−75.379 414	−99.363 827
B	−38.903 264	−55.536 052	−75.370 271	−99.363 827
C	−39.004 814	−55.689 883	−75.524 536	−99.507 612
D	−39.028 762	−55.716 614	−75.549 519	−99.530 718
E	−39.042 557	−55.735 739	−75.562 889	−99.528 794
F	−39.051 194	−55.766 119	−75.614 485	−99.598 561
G	−39.069 470	−55.790 237	−75.648 903	−99.642 288
H	−39.065 671	−55.786 457	−75.645 598	−99.639 927

[a] A = HF/6-31G(d′); B = HF/6-31G(d′)(0 K); C = MP2/6-31G(d′); D = QCISD(T)/6-31+G(d′); E = MP4/CBSB4; F = MP2/CBSB3; G = CBS-Q(0 K); H = CBS-Q; E_I = total energy for triplet CH_2; E_{II} = total energy for NH_2 radical; E_{III} = total energy for OH radical; E_{IV} = total energy for F radical.

TABLE 7: Total Energies (au) for CH_2 Carbene Fused Products and Their Enthalpy of the Reaction (kcal/mol)[a]

	E_I	E_{II}	E_{III}	ΔE_I	ΔE_{II}	ΔE_{III}
A	−94.579 859	−114.403 865	−138.396 654	63.8	64.6	69.8
B	−94.529 627	−114.365 686	−138.371 704	56.7	57.8	65.6
C	−94.861 589	−114.700 286	−138.696 028	104.7	107.3	115.2
D	−94.907 200	−114.729 185	−138.736 618	101.5	94.7	111.2
E	−94.935 705	−114.765 685	−138.746 246	98.8	100.5	109.7
F	−94.992 378	−114.847 358	−138.849 644	109.9	114.0	125.4
G	−95.023 958	−114.888 516	−138.904 056	103.1	106.8	120.7
H	−95.019 596	−114.884 242	−138.900 232	105.1	108.5	122.1

[a] A = HF/6-31G(d′); B = HF/6-31G(d′)(0 K); C = MP2/6-31G(d′); D = QCISD(T)/6-31+G(d′); E = MP4/CBSB4; F = MP2/CBSB3; G = CBS-Q(0 K); H = CBS-Q; E_I = total energy for H_2CNH_2 radical; E_{II} = total energy for H_2COH radical; E_{III} = total energy H_2CF radical; ΔE_I = enthalpy for the H_2C + NH_2 reaction; ΔE_{II} = enthalpy for the H_2C + OH reaction; ΔE_{III} = enthalpy for the H_2C + F reaction.

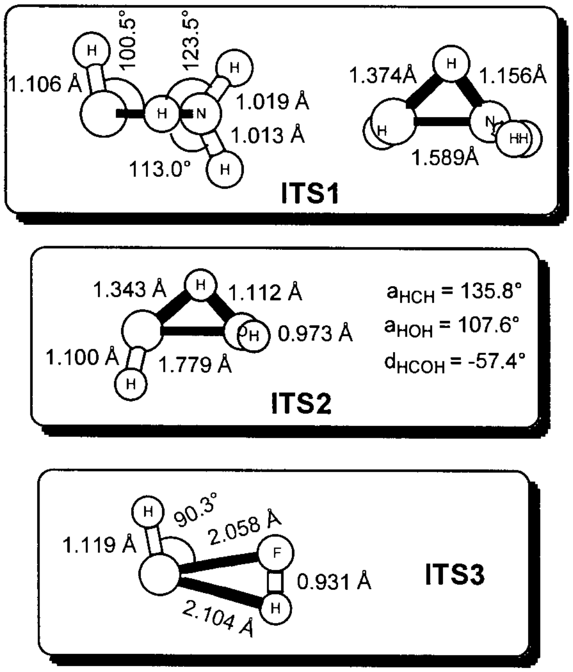

Figure 5. Transition-state structures for the CH radical insertion into ammonia, water, and hydrogen fluoride.

TABLE 8: Total Energies (au) for Transition-State Structures and Activation Barriers (kcal/mol) for the CH Radical Insertion Reactions[a]

	E_{I}	E_{II}	E_{III}	ΔE_{I}	ΔE_{II}	ΔE_{III}
A	−94.425 366	−114.235 879	−138.266 896	−15.7	−23.4	2.2
B	−94.377 618	−114.203 563	−138.245 176	−18.0	−24.8	−0.8
C	−94.713 116	−114.544 341	−138.546 551	11.6	3.7	6.9
D	−94.763 283	−114.589 652	−138.597 426	6.6	-2.6	2.6
E	−94.792 924	−114.619 360	−138.618 396	4.0	-5.5	0.9
F	−94.850 250	−114.699 345	−138.708 503	14.3	3.2	3.0
G	−94.886 351	−114.748 908	−138.772 283	9.5	0.2	0.6
H	−94.882 116	−114.744 448	−138.767 656	11.3	1.8	1.8

[a] A = HF/6-31G(d′); B = HF/6-31G(d′)(0 K); C = MP2/6-31G(d′); D = QCISD(T)/6-31+G(d′); E = MP4/CBSB4; F = MP2/CBSB3; G = CBS-Q(0 K); H = CBS-Q. The transition-state total energy for the CH radical insertion into ammonia (E_{I}), water (E_{II}), and hydrogen fluoride (E_{III}); activation barriers (kcal/mol) for the CH radical insertion reaction into ammonia (ΔE_{I}), water (ΔE_{II}), and hydrogen fluoride (ΔE_{III}).

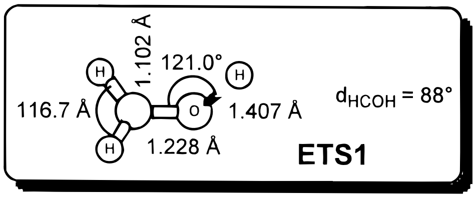

Figure 6. Transition-state structures for elimination of hydrogen radical from H_2COH radical.

insertion reaction with ammonia is around 10 kcal/mol, while for reactions with both water and hydrogen fluoride it is very close to zero. This definitely indicates that a major process in the interaction of CH radical with small polar molecules is through the insertion reaction.

The products of the insertion reaction with ammonia and water are hydrogen-bonding complexes with the hydrogen radical (Figure 4). Therefore, eliminating the hydrogen radical will result in producing stable neutral molecules. We were not able to locate a transition-state structure for hydrogen radical elimination from H_2CNH_2. The transition-state structure for hydrogen radical elimination from H_2COH is presented in Figure 6. There are noticeable structural changes of **ETS1** when compared to the H_2COH radical. With the exception of the largest change coming in the O−H distance (now 1.407 Å), the change in the C−O bond distance is now closer to the carbon−oxygen double-bond distance. The HCOH dihedral angle is changed, indicating an increase in p−p atomic orbital overlap in the course of the reaction. If we consider the dihedral angel in the transition-state structure as a measure of its position on the potential energy surface, then the transition state is very close to the product because the dihedral angle is close to 90°. Knowing that the products are considerably more stable than the reactants, one can expect that the activation barrier should be relatively high. The CBS computed activation barrier is 38.8 kcal/mol. Another possibility to form the formaldehyde and hydrogen radical is the rearrangement of the H_2COH radical into the H_3CO radical and then elimination of the hydrogen radical. The computed activation barrier for this reaction is almost identical (39.3 kcal/mol) to that of the elimination reaction. Similar observations can be obtained for the dispropotionation of H_2CNH_2 and HCFH radicals.

To confirm the reliability of the CBSQ method for computing thermodynamic properties of these chemical systems, we have evaluated heats of the reaction for several reactions involved in these studies for which experimental data[17] are available (Table 9). All computed heats of the reaction are in perfect agreement with experimental values, suggesting that all computed energies presented in this paper are highly accurate. Recently, the CH complexation energy with ammonia, water, and hydrogen fluoride was computed at the MP4SDTQ/6-311++G(2d,2p)//MP2/6-311++G(d,p) theory level.[18] The computed energies are 1−2 kcal/mol higher than the CBSQ computed energies. We believe that our CBSQ computed values are the more accurate ones.

TABLE 9: Heat of the Reaction (kcal/mol) for Several Chemical Reactions Studied Here

reaction	CBSQ	CBSQ(0 K)	exp
$CH + NH_3 \rightarrow CH_2 + NH_2$	7.5	7.2	7.0
$CH + NH_3 \rightarrow CH_2NH + H$	−58.6	−58.0	−53.0
$CH + H_2O \rightarrow CH_2OH$	−89.0	−87.8	−86.2
$CH + H_2O \rightarrow CH_2 + OH$	19.0	18.9	17.6
$CH + H_2O \rightarrow CH_3O$	−79.5	−77.6	−80.7
$CH + H_2O \rightarrow CH_2O + H$	−59.5	−63.3	−60.0

Conclusion

On the basis of the results presented in this paper, it can be concluded that the complete ab initio method is highly accurate for the evaluation of thermodynamic properties of such small chemical systems. It was determined that a hydrogen radical between the CH radical and neutral molecules such as ammonia, water, and hydrogen fluoride is possible and is occurring with a very small activation barrier, but it is not leading to the formation of desirable products. Fusion of the formed radicals is not energetically preferred. The same is true for fusing the CH radical and neutral molecules. The reaction that has little or no activation barrier at all is insertion of the CH radical. Formed insertion product is further stabilized through hydrogen elimination. All computed energies are in excellent agreement with the experimental data where available.

References and Notes

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