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Response to Comment on "High-Level ab Initio and Density Functional Study of the CH + NO Reaction Product Branching"

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In their Comment,[1] East and Allen were comparing computed thermodynamic values for some CH + NO branching reactions earlier reported by them[2] to those which were reported by us.[3] The comparison was also made with the best experimental values currently available.[4−8] Besides those already mentioned computational studies for the title reaction, there are many previous ab initio studies performed at various theory levels.[9] In our original paper, the computational studies were performed with the two highly accurate G2 and CBSQ ab initio approaches for computing thermodynamic properties and the hybrid density functional B3LYP methods that is contrary two to these ab initio approaches applicable to larger chemical systems than studied in this paper.[3] Considering the reliability and broad use of these two ab initio approaches, we had stated that we believe that the computed values are of more accuracy than some of the currently used values. Even in their incomplete comparison, East and Allen agree that both G2 and CBSQ methods compute reliable energies.

Contrary to East and Allen's comments, the target of our studies was not to compare our computational results with theirs or anybody else's, but rather our G2 and CBSQ ab initio on the one hand and B3LYP density functional on the other hand with the available experimental results. In this way, we demonstrate that both G2 and CBSQ can compute reliable thermodynamic properties for the CH + NO reaction product branching and offer some new values that can be used by experimentalists when these reactions were to be studied. From very many of our computational results we know that B3LYP computes thermodynamic properties of various chemical systems that are ±3.0 kcal/mol away from the experimental values. Because in many combustion and atmospheric reactions multispin chemical systems are involved, some of the ab initio methods show problems with computing appropriate energies due to substantial spin contamination. Contrary to that, the B3LYP density functional theory method in general does not have this problem. Therefore, it is of importance for researchers in those fields that explore relatively large chemical systems that the B3LYP can be practical for computational study and at the same time produce reliable energies.

To the best of our knowledge, there are no studies of this kind prior to our report performed on the CH + NO reaction. Therefore, our reported results cannot supersede any results. It is mentioned that results obtained with G2 and CBSQ can be considered superfluous. Many scientists in physical chemistry have used these two methods successfully to compute thermodynamic properties for various chemical systems. Furthermore, the authors state that their comparison with our results is the "best interpretation of the baffling listing by Jursic of single-state energies for multistate products". This is a very interesting conclusion made because from our paper at the end of the computational methods section we state "The energy computed in this paper is for the lower lying triplet or singlet of the products". In the abstract as well as in the conclusion part of our paper,[3] we clearly outline for what branching product and in what multiplicity thermodynamic properties are computed. For instance, the abstract of our paper ends with the sentence "The suggested CBSQ enthalpies at 298 K for the CH + NO branching reaction are −3.47 eV for H(^{2}S) + NCO(X$^2\Pi$, A$^2\Sigma^+$), ..., and −1.01 eV H(^{2}S) + N(^{2}S) + N(^{2}S) + CO(X$^1\Sigma^+$)." Clearly, the temperature as well as the electronic state for every product was outlined and there should be no misunderstanding. Furthermore, East and Allen[1] in their Table 2 state "Zero kelvin assumed". For our calculations, in each and every one of our tables listing energies, we state "(0 K) = sum of electronic and zero-point energies, the ab initio computed energies are 298 K and 1 atm." Therefore, there is nothing there to be assumed.

TABLE 1: Comparison of Computed and Experimental Enthalpies (kcal/mol) for HNCO and ^{2}NCO Formation and for H−N and the N−C Bond Breaking in the HNCO[a]

theory	ΔH^0_f(HNCO)	ΔH^0_f(^{2}NCO)	BDE(I)	BDE(II)
B3LYP[3]	−27.8	27.0	106.7	88.0
G2[3]	−30.2	27.5	109.9	86.0
CBSQ[3]	−29.0	28.3	109.6	87.4
CCSD[1,2]	−27.5	31.4	110.5	86.8
exp	−27.8, −27.7	30.3, 30.5	109.7, 110.1	86.0

[a] Density functional theory computational studies were all performed with the 6-311G(2d,2p) basis set and energies are reported at 0 K; ΔH^0_f (HNCO) = enthalpy of the HNCO formation; ΔH^0_f (^{2}NCO) = enthalpy formation for ^{2}NCO; BDE(I) = enthalpy for HNCO → ^{2}H + ^{2}NCO; BDE(II) = enthalpy for HNCO → ^{3}HN + ^{1}CO.

For an appropriate comparison between the B3LYP and CCSD, the same basis set should be used. Furthermore, there are several of the experimental values listed in their Table 1.[1] One is for energy that we have not computed. What set of experimental results were used for calculation of average absolute error listed in their Table 1? For practical reasons one should agree that there are no substantial differences between G2, CBSQ, and their estimated energies (our Tables 1 and 2). Considering that the CBSQ ab initio method has the least computational demand it should be a method of choice for computing this and similar chemical systems. As demonstrated in both tables that contain a selected thermodynamic properties extracted from our[3] and East and Allen[1,2] computational results, the CBSQ computed energies well agree with the experimental as well CCSD ab initio values. On the other hand, the B3LYP computed energies are known to have a larger computational error (±3 kcal/mol). If we consider this computational error it is conceivable that the B3LYP computed values are also in good agreement with both CBSQ and experimental energies where available (our Tables 1 and 2).

In short, the East/Allen comments[1] on our results previously presented[3] are unfounded. Many "assumptions" made by the authors of the comments cannot be withdrawn from our paper. There is nothing "superfluous" in our results, and the multiplicity (electronic states) for molecular species as well as temperature at which the energies are computed are clearly explained in our paper.[3] There are no "miscalculations" reported and there is not any desire that our results are considered as one that supersede East/Allen's or anybody else's. It was clearly stated that listed values in the abstract of the paper[3] are CBSQ values computed at 298 K and they are "suggested". All theoretical approaches

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TABLE 2: Comparison of Computed Enthalpies[a] (kcal/mol) for Some H/N/C/O Reactions

theory	Δ*H*(I)	Δ*H*(II)	Δ*H*(III)	Δ*H*(IV)	Δ*H*(V)	Δ*H*(VI)	Δ*H*(VII)	Δ*H*(VIII)	Δ*H*(IX)
B3LYP[3]	−83.9	−102.8	−70.1	−44.3	−39.9	68.1	28.2	−91.0	−62.8
G2[3]	−80.9	−104.9	−71.7	−46.6	−40.4	68.6	25.4	−84.4	−59.9
CBSQ[3]	−81.9	−104.0	−71.3	−47.5	−40.6	68.2	25.8	−85.5	−59.7

[a] All energies are computed at 0 K; Δ*H*(I) = enthalpy for $^2CH + ^2NO \rightarrow ^2H + ^2NCO$; Δ*H*(I) = enthalpy for $^2CH + ^2NO \rightarrow ^2H + ^2NCO$; Δ*H*(II) = enthalpy for $^2CH + ^2NO \rightarrow ^3NH + ^1CO$; Δ*H*(III) = enthalpy for $^2CH + ^2NO \rightarrow ^3O + ^1HCN$; Δ*H*(IV) = enthalpy for $^2CH + ^2NO \rightarrow ^2OH + ^2CN$; Δ*H*(V) = enthalpy for $^2CH + ^2NO \rightarrow ^4N + ^2HCO$; Δ*H*(VI) = enthalpy for HNCO → HCNO; Δ*H*(VII) = enthalpy for HNCO → HOCN; Δ*H*(VIII) = enthalpy for c-HCNO → HNCO; Δ*H*(IX) = enthalpy for c-HCNO → HOCN.

that are used by us and East/Allen have some kind of approximations. It seems appropriate to be reminded that only good experimental values are accurate and regardless of what theory level is used for generating computational values, they are always “estimates”. The estimates are good as they agree to a certain degree with the experiment. Our presented results belong to this category.

References and Notes

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