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Comment on “High-Level ab Initio and Density Functional Study of the CH + NO Reaction Product Branching”

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In this paper, Jursic[1] has disregarded several earlier studies already detailing the thermochemistry of the four-atom H/N/C/O system. Descriptions of the isomerization and fragmentation pathways and transition states are already well documented.[2−4] Furthermore, Jursic claims that the branching reaction thermochemistry for CH + NO had not been accurately determined prior to his work and believes that his computed energies are the best ones. We wish to provide evidence to the contrary. Our own theoretical work in 1993[5,6] resulted in a thermochemical ladder of HNCO isomers and fragments (Figure 1 of ref 3) accurate to the 1 kcal mol^{-1} level. Several experimental groups, particularly those of Wittig,[7] Crim,[8] and Reisler,[9,10] have since solidified the thermochemistry of HNCO photodissociation, and their results clearly demonstrate the accuracy of our 1993 ladder, as can be seen in Table 1. The tabulations of Jursic might thus be considered superfluous, since *all* of his sets of results (including G2 and CBSQ) appear to be less accurate than ours. In Table 2 additional comparisons are made between CH + NO reaction enthalpies and HNCO isomerization energies of Jursic[1] and us.[6] These comparisons assume our best interpretation of the baffling listing by Jursic of single-state energies for multistate products, reminiscent of previous Jursic miscalculations.[13,14] His G2 and CBSQ values in our Table 2 appear as accurate as in Table 1, excluding the reaction to HO + CN, which along with his reaction to H + CNO may warrant further investigation. In summary, the 1993 results which Jursic does not cite have not been superseded by his recent computations.

TABLE 1: Comparison of Theoretical Results for HNCO Thermochemistry (kcal mol^{-1})[a]

	B3LYP[b]	G2[b]	CBSQ[b]	East/Allen[c]	expt
ΔH^0_f(HNCO)	−27.8	−30.2	−29.0	−27.5	−27.8(4)[d] −27.7(11)[e]
ΔH^0_f(NCO)	27.0	27.5	28.3	31.4	30.3(4)[d] 30.5(10)[f]
D_0(H + $^2\Pi$ NCO)	106.7	109.9	109.6	110.5	109.7(1)[d] 110.1(3)[g]
D_0($^3\Sigma^-$ HN + CO)	88.0	86.0	87.4	86.8	85.95(7)[h]
D_0($^1\Delta$ HN + CO)				122.6	122.23(7)[h] 122.1(3)[e]
av abs error	2.1	1.4	1.2	0.7	

[a] Zero kelvin values. [b] Reference 1. [c] Reference 6, based on CCSD(T) and bond-additivity corrections. [d] Reference 9. [e] Reference 8. [f] Reference 11. [g] Reference 12. [h] Reference 10.

TABLE 2: Comparison of Theoretical Reaction and Isomerization Enthalpies (kcal mol^{-1})[a]

reaction[b]	B3LYP[c]	G2[c]	CBSQ[c]	East/Allen[d]
CH + NO → H + NCO	−83.9	−80.9	−81.9	−79.6
CH + NO → NH + CO	−102.8	−104.9	−104.0	−103.3
CH + NO → O + HCN	−70.1	−71.7	−71.3	−71.7
CH + NO → OH + CN	−44.3	−46.6	−47.5	−50.1
CH + NO → N + HCO	−39.9	−40.4	−40.6	−39.7
HNCO → HCNO	68.1	68.6	68.2	69.1
HNCO → HOCN	28.2	25.4	25.8	25.4

[a] Zero kelvin values. [b] Ground states only. The radical ground states are ^{2}S(H), ^{3}P(O), ^{4}S(N), ^{2}A′(HCO), $^2\Pi$(NCO, CH, NO, OH), $^2\Sigma^+$(CN), $^3\Sigma^-$(NH). [c] Reference 1. [d] Reference 6, based on CCSD(T) and bond-additivity corrections.

References and Notes

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