

A NEW PATH TO "PROMPT" NO: CH + N₂ = H + CN STUDIED BY AB INITIO MO AND STATISTICAL THEORY CALCULATIONS

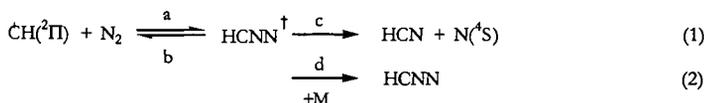
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ABSTRACT

In the past two decades, the CH(²Π) + N₂ → HCN + N(⁴S) reaction has been routinely employed for kinetic modeling of NO_x formation in hydrocarbon combustion. The reaction has been studied by many investigators¹⁻¹⁷ since Fenimore¹⁸ suggested it to be a potential "prompt" NO precursor process in 1971. The result of a recent comprehensive study by Morokuma and co-workers,^{19,20} however, indicated that the theoretically predicted rate constant for the formation of the spin-forbidden HCN + N products is about two orders of magnitude lower than experimentally measured values.^{1,2,7,8} The result of our high-level molecular orbital study aided by a statistical-theory calculation reveals that the spin-allowed H + NCN products occurring by the ground electronic doublet surface is the dominant CH + N₂ process under combustion conditions.

INTRODUCTION

The kinetics of the reaction available prior to 1983 were first interpreted in terms of the global mechanism involving an internally excited HCNN adduct:



by Berman and Lin,⁴ who measured the pressure-dependent bimolecular rate constant (*k*₂) by laser-induced fluorescence, monitoring the decay of CH at temperatures between 297 and 675 K. Their low-temperature, pressure-dependent data, which have been corroborated in subsequent independent studies,^{9,10} were correlated with high-temperature NO formation results by Blauwens et al.¹ with the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. More recently, there have been two shock-tube studies at high temperatures, monitoring either CH decay by laser absorption spectroscopy or N production by atomic resonance absorption spectroscopy, providing the much needed high-temperature kinetic data.^{7,8}

Theoretically, the production of N atoms by reaction (1) has been investigated by Manna and Yarkony^{13,14} on the nature of the doublet-quartet curve crossing and by Walch¹⁵ and Seideman and Walch¹⁶ on the potential energy surface (PES) involved. Miller and Walch¹⁷ recently calculated *k*₁, ignoring the retarding effect of the doublet-quartet crossing, with the RRKM theory above 1000 K and concluded that the high-temperature shock-tube data of Hanson, Roth and co-workers^{7,8} can be satisfactorily accounted for. On the other hand, the result of a more comprehensive calculation by Morokuma and co-workers²⁰, based on a more detailed PES¹⁹ with the inclusion of the curve crossing effect, indicated a rather poor agreement between theory and experiment as alluded to above.

RESULTS AND DISCUSSION

In this work, we study the mechanism of the CH + N₂ reaction, centering on the reaction path over the ground electronic doublet PES. The result of this high-level *ab initio* molecular orbital calculation, aided by a multichannel RRKM analysis and kinetic modeling for CH decay and N production reveals unambiguously that the prompt NO observed in hydrocarbon flames actually arises primarily from the spin-allowed reaction,



The reaction occurs via two NC(H)N ring intermediates and the HNCN radical. The prompt NO can be formed by the facile, exothermic oxidation of NCN by O, OH and O₂ present in the flame.

The PES of the ground electronic doublet state, shown in Fig. 1 with a relevant portion of the quartet state leading to HCN + N, has been computed with the G2M method.²¹ The method employed is the same as previously used by Cui and Morokuma.¹⁹ The geometries were

optimized at the B3LYP level (Becke's three parameter density functional²² with the nonlocal correlation functional of Lee, Yang, and Parr²³) with the standard 6-31G(d,p) basis set. The vibrational frequencies used for characterization of stationary points, ZPE corrections and RRKM calculations, were computed at the same level of theory. All MO calculations were performed with the Gaussian 94²⁴ and MOLPRO96²⁵ program packages.

The quartet portion of the potential energy surface is entirely taken from ref. 19. On the doublet surface we found a concerted path connecting a ring intermediate, INT2, with the HNCN radical, the latter can dissociate to H + NCN. The endothermicity of this channel is 21.5 kcal/mol at the G2M level, while the concerted transition state, TS3, is 11.7 kcal/mol above the reactants at the same level of theory. The connections of this transition state to respective minima on the PES were established by an IRC test.²⁶

Since for the last part of the potential energy surface (HNCN dissociation) no distinct transition state could be found, we mapped out a one dimensional dissociation profile at the B3LYP level and fitted it with Morse potential, adjusting D_e to the respective G2M value afterwards. The resulting potential can be effectively represented by the equation, $V(r) = D_e(1 - e^{-\beta(r-r_0)})^2$, where $D_e = 84.01$ kcal/mol, $\beta = 3.27$, $r_0 = 1.160$ Å. A canonical variational RRKM calculation was performed based on the G2M energies and calculated B3LYP molecular parameters at each point along the dissociation curve for HNCN \rightarrow H + NCN.

Although the doublet product channel, NCN + H, is 18.1 kcal/mol higher than HCN + N, it is 0.8 kcal/mole lower than the last barrier leading to the formation of the latter products on the quartet surface. The apparent barrier for the HNCN dissociation would be much lower at high temperatures because of the entropic contribution, which reduces the values of ΔG^\ddagger as the temperature increases. The theoretically predicted heat of formation for the NCN radical at 0 K based on reaction (3), 111.0 kcal/mol, is in good agreement with the recently reported experimental values: by Neumark and co-workers²⁷, 111.3 kcal/mol, and by Clifford et al.²⁸, 107.4 ± 3.2 kcal/mol.

The rate constant for the production of NCN by reaction (3) was calculated with a multichannel RRKM program previously used in our study of the NH₂ + NO reaction.²⁹ The result of the calculation compares closely with those measured at high temperatures purportedly for k_1 , based on either the decay of CH⁵ or the formation of N.⁷ In the temperature range, 1500-4000 K, the predicted k_3 at 0.88 atm can be represented by the modified Arrhenius expression, $k_3 = 2.22 \times 10^7 T^{4.48} \exp(-11760/T)$ cm³/(mol·s).

SUMMARY AND CONCLUSIONS

To conclude, we have demonstrated that the CH + N₂ \rightarrow H + NCN reaction, which occurs over the ground electronic doublet PES, is spin-allowed and more favorable than the accepted, spin-forbidden path producing HCN + N. The computed rate constant for CH decay agrees quantitatively with experimentally measured values.⁸ In addition, the predicted N-atom production rate also agrees fully with experimental result⁷ within the scatter of typical shock-tube data. Under combustion conditions, NO can be formed readily by the rapid oxidation of NCN by O, OH and O₂.

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REFERENCES

1. Blauwens, J., Smets, B. & Peeters, J. *Combust. Inst.* **16**, 1055-62 (1977).
2. Matsui, Y. & Nomaguchi, T. *Combust. Flame*, **32**, 205-14 (1978).
3. Butler, J. E., Goss L. P., Lin, M. C. & Hudgens, J. W. *Chem. Phys. Lett.* **63**, 104-7 (1979).
4. Berman, M. R., Lin, M. C. *J. Phys. Chem.* **87**, 3933-42 (1983).
5. Duncanson, J. A., Jr., Guillory, W. A. *J. Chem. Phys.* **78**, 4958-62 (1983).
6. Matsui, Y. & Yuuki, A. *Jpn. J. Appl. Phys.* **24**, 598-603 (1985).
7. Lindackers, D., Burmeister, M., Roth, P. *Combust. Inst.* **23**, 251-57 (1991).
8. Dean, A. J., Hanson, R. K. & Bowman, C. T. *Combust. Inst.* **23**, 259-65 (1991).

9. Becker, K. H., Engelhardt, B., Geiger, H., Kurtenbach, R., Schrey, G. & Weisen, P. *Chem. Phys. Lett.* **195**, 322-328 (1992).
10. Medhurst, L. J., Garland, N. L. & Nelson, H. H. *J. Phys. Chem.*, **97**, 12275 (1993).
11. Morley, C. *Combust. Flame*, **27**, 189-204 (1976).
12. Miller, J. A., Bowman, C. T. *Prog. Energy Combust. Sci.*, **15**, 287-338 (1989).
13. Manna, M. R. & Yarkony D. R. *J. Chem. Phys.* **95**, 1808-1816 (1991).
14. Manna, M. R. & Yarkony D. R. *Chem. Phys. Lett.* **188**, 352-358 (1991).
15. Walch, S. P. *Chem. Phys. Lett.* **208**, 214-18 (1993).
16. Seideman, T. & Walch, S. P. *J. Chem. Phys.* **101**, 3656-61 (1994).
17. Miller, J. A., Walch, S. P. *Int. J. Chem. Kinet.* **29**, 253-259 (1996).
18. Fenimore, C. P. *Proc. Combust. Inst.* **13**, 373-79 (1971).
19. Cui, Q., Morokuma, K. *Theor. Chem. Acc.* **102**, 127-133 (1999).
20. Cui, Q., Morokuma, K., Bowman, J. M., and Klippenstein, S. *J. Chem. Phys.* **110**, 9469-82 (1999).
21. Mebel, A. M., Morokuma, K. & Lin, M. C. *J. Chem. Phys.* **103**, 7414-21 (1995).
22. Becke, A. D. *J. Chem. Phys.* **98**, 5648-52 (1993).
23. Lee, C., Yang, W. & Parr, R. G. *Phys. Rev. B*, **37**, 785-9 (1998).
24. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *GAUSSIAN 94, REVISION A.1*; Gaussian, Inc., Pittsburgh PA, 1995.
25. MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H. Stoll and T. Thorsteinsson.
26. Gonzalez, C. Sosa, C., and Schlegel, H. B. *J. Phys. Chem.* **93**, 2435-40 (1989).
27. Bise, R. T., Choi, H., Neumark, D. H. *J. Chem. Phys.* **111**, 4923-32 (1999).
28. Clifford, E. P., Wenthold, P. G., Lineberger, W. C., Petersson, G., and Ellison, G. B. *J. Phys. Chem.* **101**, 4338-45 (1997).
29. Diau, E. W., Wagner, M. A. G. & Lin, M. C. *J. Phys. Chem.* **98**, 4034-42 (1994).

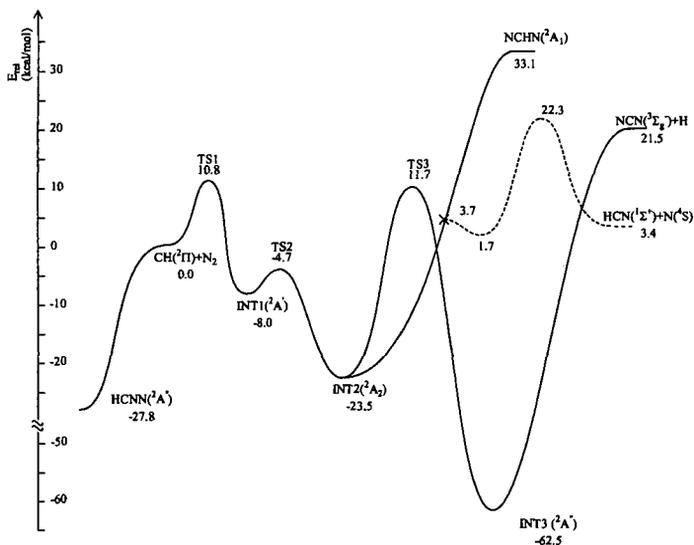


Figure 1. Potential energy diagram for reaction (3) combining the result of Cui and Morokuma¹⁹ for the quartet state given by the dotted curve where "x" indicates curve crossing with the present work for the doublet state given by the solid curve. The relative energies are calculated at the G2M(RCC) level including B3LYP/6-311g(d,p) ZPE correction.