

Characterization of the minimum energy path for the reaction of singlet methylene with N₂: The role of singlet methylene in prompt NO

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We report calculations of the minimum energy pathways connecting ¹CH₂+N₂ to diazomethane and diazirine, for the rearrangement of diazirine to diazomethane, for the dissociation of diazirine to HCN₂+H, and of diazomethane to CH₂N+N. The calculations use complete active space self-consistent field (CASSCF) derivative methods to characterize the stationary points and internally contracted configuration interaction (ICCI) to determine the energetics. The calculations suggest a potential new source of prompt NO from the reaction of ¹CH₂ with N₂ to give diazirine, and subsequent reaction of diazirine with hydrogen abstractors to form doublet HCN₂, which leads to HCN+N(⁴S) on the previously studied CH+N₂ surface. The calculations also predict accurate 0 K heats of formation of 77.7 kcal/mol and 68.0 kcal/mol for diazirine and diazomethane, respectively. © 1995 American Institute of Physics.

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I. INTRODUCTION

The reaction of singlet methylene (¹CH₂) with N₂ along with the reaction of CH(²Π) with N₂, which was previously studied by Walch,¹ are potentially important in the formation of "prompt" NO.² While triplet methylene is known to be important in some of the reactions leading to prompt NO formation,² the role of singlet methylene has not been considered previously. There have been several previous studies of the CH₂N₂ surface. An early study of the ground state and some of the low-lying excited states of diazomethane, at the ground state geometry, was carried out by Walch and Goddard.³ More recent work has been carried out by Boldyrev, Schleyer, Higgins, Thomson, and Kramarenko⁴ (BSHTK) who studied the diazirine and diazomethane minima and several saddle points on the CH₂N₂ as well as the CHF₂N₂ and CF₂N₂ potential energy surfaces. Guimon, Khayar, Gracian, Begtrup, and Pfister Guillouzo⁵ (GKGBP), as part of a study on the decomposition of tetrazole, also reported a number of stationary points on the CH₂N₂ surface, including a saddle point connecting diazirine and diazomethane. These studies were carried out at a lower level of theory than that used in the present study and did not provide sufficiently detailed information for combustion modelling studies. In this paper we report a detailed study of the pathways for addition of ¹CH₂ to N₂ to give diazomethane and diazirine and the pathway for rearrangement of diazirine to diazomethane. Calculations with extended basis sets are also reported which lead to accurate heats of formation for diazirine and diazomethane.

In Sec. II we discuss qualitative features of the reactions considered here. Section III contains the technical details of the calculations, Sec. IV contains the results, and Sec. V concludes the paper.

II. QUALITATIVE FEATURES

Figure 1 shows the qualitative features of the orbitals for the reaction of ¹CH₂ with N₂ via a pathway in which the CH₂ attacks the π bond of N₂. In the ¹A₁ ground state of methylene (¹CH₂) there is a substantial near degeneracy effect

between the C 2s lone pair and the empty C 2p orbital of a'' symmetry. This leads to a pair of singlet coupled sp hybrid orbitals directed above and below the molecular plane, as indicated in Fig. 1(a). In the addition of ¹CH₂ to N₂, two bond pairs undergo major changes. These are the two electrons in the CH₂ C 2s pair discussed earlier and the in plane π orbital of N₂. By analogy to the reaction of CH(²Π) with N₂ (Ref. 1) and the reaction of CH(²Π) with H₂ (Ref. 6), the addition of ¹CH₂ to N₂ occurs via a pathway, as shown in Fig. 1(a), in which the CH and N₂ approach each other in a

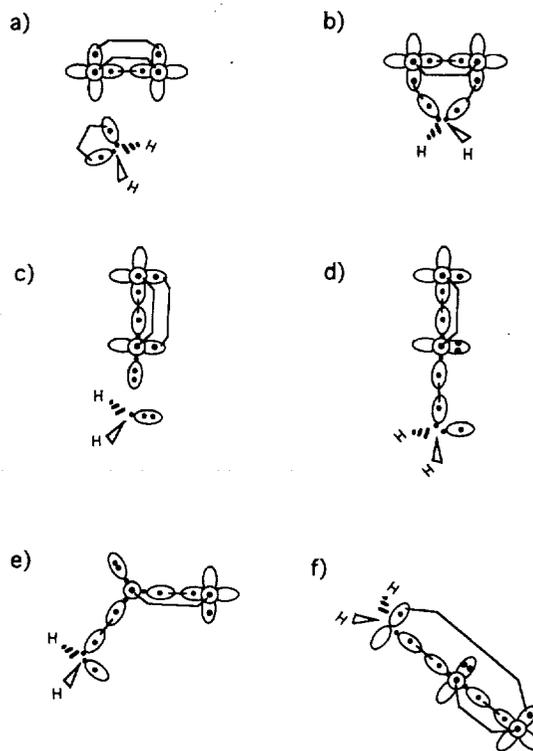


FIG. 1. The electronic structure of selected stationary points on the potential energy surface for CH₂(¹A₁)+N₂: (a) sp₁; (b) min 1; (c) sp₃; (d) distorted diazomethane; (e) sp₂; (f) min 2.

TABLE I. Computed energies for stationary points on the ¹CH₂+N₂ surface.

| Geometry | CII ^a | ΔE ^b | | |
|--|------------------------|------------------|------------------------|-----------------|
| | | (a) ^c | | |
| Reactants | -148.427 21(-0.469 40) | 0.0 | | |
| min 1 | -148.471 56(-0.518 97) | -24.0 | | |
| min 2 | -148.480 05(-0.531 98) | -33.9 | | |
| ³ CH ₂ +N ₂ | -148.443 88(-0.484 81) | -9.7 | | |
| Geometry | CII ^a | ΔE ^b | CI2 ^a | ΔE ^b |
| | | (b) ^d | | |
| Reactants | -148.391 06(-0.43026) | 0.0 | -148.392 69(-0.431 14) | 0.0 |
| ³ CH ₂ +N ₂ | -148.408 70(-0.44677) | -10.4 | | |
| vdW | -148.390 96(-0.43381) | -0.5 | | |
| sp3 | -148.398 69(-0.44458) | -4.9 | | |
| sp1 | -148.383 37(-0.42918) | 4.7 | -148.385 66(-0.430 64) | 4.4 |
| min 1 | -148.434 44(-0.47866) | -23.3 | -148.435 68(-0.479 61) | -23.3 |
| sp2 | | | -148.359 65(-0.405 59) | 19.8 |
| min 2 | -148.443 45(-0.49145) | -32.9 | | -33.2 |
| CH ₂ N+N | | | -148.291 37(-0.332 44) | 64.3 |
| HCN ₂ +H | -148.282 39(-0.32161) | 66.2 | | |
| Geometry | CII ^a | ΔE ^b | | |
| | | (c) ^e | | |
| Reactants | -148.270 49(-0.29892) | 0.0 | | |
| min 1 | -148.311 75(-0.34441) | -21.4 | | |
| min 2 | -148.319 34(-0.35505) | -29.7 | | |
| ³ CH ₂ +N ₂ | -148.290 72(-0.31842) | -12.3 | | |
| Geometry | CASSCF | ΔE ^a | | |
| | | (d) | | |
| Reactants | -147.998 52 | 0.0 | | |
| sp1 | -147.967 61 | 23.5 | | |
| min 1 | -148.015 41 | -3.5 | | |
| sp2 | -147.939 63 | 40.8 | | |
| min 2 | -148.011 55 | -2.7 | | |
| vdW | -148.004 30 | -1.9 | | |
| sp3 | -148.001 51 | 2.2 | | |

^aThe energies are in the form ICCI (ICCI+Q+148).

^bRelative energies in kcal/mol including zero-point energy (see Table II).

^ccc-pVQZ basis set.

^dcc-pVTZ basis set.

^ecc-pVDZ basis set.

nearly parallel arrangement. This non-least-motion pathway allows the formation of the diazirine molecule [Fig. 1(b)], while maintaining large overlaps between the components of the two bond pairs which change substantially during the course of the reaction (see Ref. 6). By contrast, addition of ¹CH₂ to N₂ via a C_{2v} pathway requires effectively breaking one bond and is a forbidden process.⁷

Another pathway leading to diazomethane involves initial formation of a dative bond between one N 2s lone pair of N₂ and the empty C 2p orbital of CH₂ [Fig. 1(c)]. This structure evolves to diazomethane [Fig. 1(d)] by simultaneous donation of the N 2s pair onto carbon and back donation of the C 2s pair into the π system of diazomethane. This process involves no barrier.

Figure 1(e) shows the orbitals for the saddle point connecting diazirine to diazomethane. The two radical orbitals in Fig. 1(e) arise from the CN σ bond of diazirine which is being broken. The doubly occupied orbital on the center N

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III. COMPUTATIONAL DETAILS

Several different basis sets were used in these calculations. For the CASSCF derivative calculations, which were used to locate the stationary points, the polarized valence double zeta set of Dunning and Hay⁸ was used. The basis sets for C and N are the (9s5p)/[3s2p] basis augmented by a single set of 3d functions with exponent 0.75 for C and

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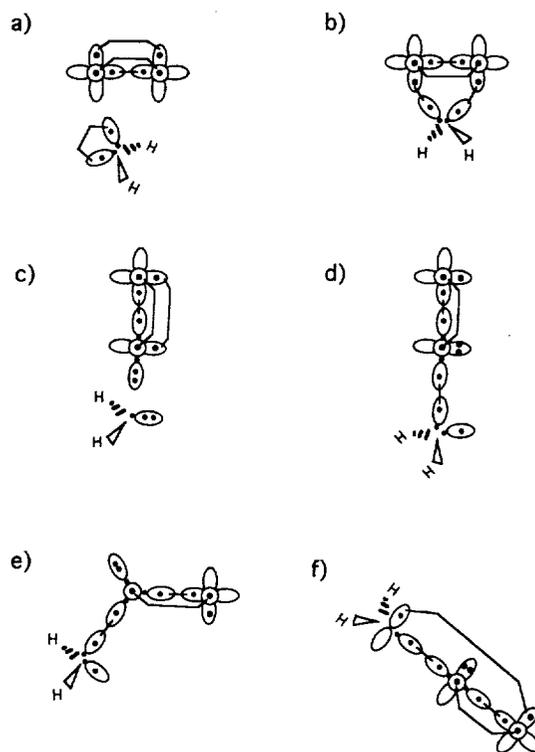


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TABLE II. Harmonic vibrational frequencies and zero-point energy for ¹CH₂+N₂. Harmonic frequencies in cm⁻¹ obtained from CASSCF calculations with a pVDZ basis set.

| | <i>sp1</i> | vdW | min 1 | <i>sp2</i> | min 2 | CH ₂ N | HCN ₂ |
|------------------|------------|----------|----------|--------------|----------|-------------------|------------------|
| Frequencies | | | | | | | |
| 3214 | | 3100 | 3307 | 3313 | 3360 | 3253 | 3432 |
| 1951 | | 2329 | 1660 | 1595 | 1902 | 1659 | 1570 |
| 1461 | | 1509 | 1546 | 1491 | 1495 | 1438 | 612 |
| 1081 | | 534 | 1033 | 960 | 1162 | 1001 | 928 |
| 477 | | 97 | 1047 | 747 | 560 | 3360 | 1251 |
| 721 <i>i</i> | | 75 | 836 | 888 <i>i</i> | 328 | 1021 | 891 |
| 3348 | | 3176 | 3436 | 141 | 3505 | | |
| 1009 | | 373 | 1166 | 3458 | 1188 | | |
| 389 | | 80 | 1018 | 1047 | 419 | | |
| ZPE ^a | | | | | | | |
| | 0.029 45 | 0.025 68 | 0.034 28 | 0.029 05 | 0.031 71 | 0.026 73 | 0.019 76 |
| <i>sp3</i> | | | | | | | |
| 3142 | | | | | | | |
| 2342 | | | | | | | |
| 1471 | | | | | | | |
| 1180 | | | | | | | |
| 258 | | | | | | | |
| 248 <i>i</i> | | | | | | | |
| 3240 | | | | | | | |
| 1084 | | | | | | | |
| 232 | | | | | | | |
| ZPE ^a | | | | | | | |
| | 0.029 50 | | | | | | |

^aZero-point energy in E_H . The zero-point energy for the reactants is 0.022 97.

0.80 for N (pVDZ). The H basis is (4*s*)/[2*s*] augmented with a single set of 2*p* functions with exponent 1.00. The basis sets used in ICCI calculations are the Dunning correlation consistent cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets.⁹

The calculations were carried out in C_s symmetry with the mirror plane in the plane of the paper of Fig. 1. The active space for the CASSCF calculations included the eight electrons which are depicted in Fig. 1(a). This required six active orbitals of *a'* symmetry and two active orbitals of *a''* symmetry. The resulting CASSCF calculation had eight electrons distributed among eight orbitals.

The CASSCF gradient calculations used the SIRIUS/ABACUS system of programs,¹⁰ while the ICCI calculations were carried out with MOLPRO.^{11,12} All electrons were correlated except for the C 1*s* and N 1*s* like electrons with the restriction that no more than two electrons were allowed into certain weakly occupied orbitals. These orbitals were the highest three *a'* and highest *a''* orbitals for the calculation denoted by CI1 and the highest two *a'* and highest *a''* orbitals for the calculation denoted by CI2. A multireference analog of the Davidson's correction¹³ was added to the ICCI energies and is denoted by +*Q*.

IV. DISCUSSION

The computed ICCI energies obtained at the optimized CASSCF geometries are given in Tables I(a), I(b), and I(c) for results obtained with the cc-pVQZ, cc-pVTZ, and cc-pVDZ basis sets, respectively. The zero-point effects were estimated as 1/2 the sum of the harmonic frequencies, which are given in Table II, and the zero-point effects are included in the relative energies, which are also given in Tables I(a)–

I(c). Thus, the relative energies are appropriate for comparison to experimental results corrected to 0 K. The relative energies from Table I are also shown in Fig. 2. Table III gives the values of selected bond lengths and angles for the stationary points obtained here and also gives results from

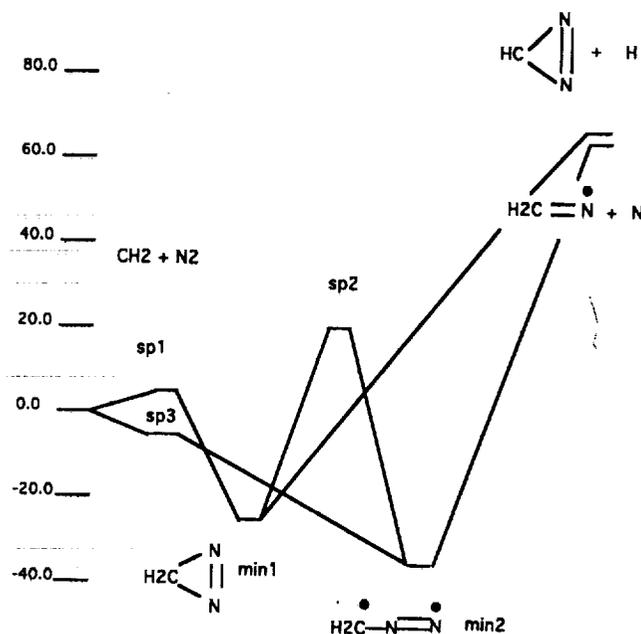


FIG. 2. Computed energetics for the reaction of CH₂(¹A₁) with N₂. Note that while *sp3* is a saddle point at the CASSCF level, it is below the reactants energy at the ICCI level and it is probable that there is no barrier on this pathway.

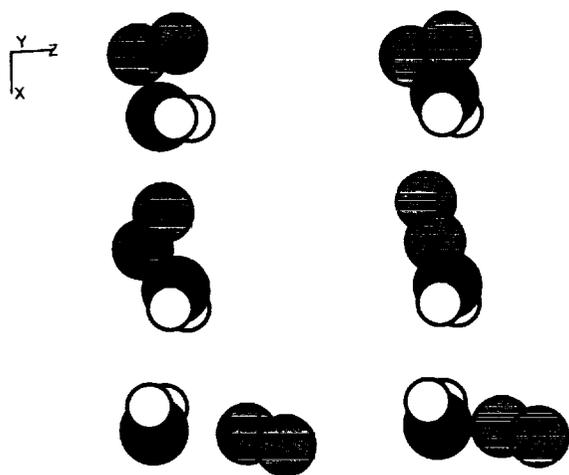


FIG. 3. Geometries for the stationary points on the $^1\text{CH}_2+\text{N}_2$ surface. Upper left sp_1 ; upper-right min 1; center left sp_2 ; center right min 2; bottom left vdW; bottom-right sp_3 .

omethane and 34.1 kcal/mol for diazirine. These values include zero-point effects and are appropriate for 0 K. Using a heat of formation of $^1\text{CH}_2$ of 102.1 kcal/mol obtained from the heat of formation of $^3\text{CH}_2$ of 93 kcal/mol and a singlet-triplet splitting of 9.1 kcal/mol gives heats of formation of 77.7 kcal/mol for diazirine and 68.0 kcal/mol for diazomethane. Laufer and Okobe¹⁷ report the heat of formation of diazirine as 60.6–66 kcal/mol. However, there is an earlier value of 79.3 kcal/mol by Paulett and Ettinger.¹⁸ The discrepancy between our calculated value and the value of Laufer and Okobe is surprisingly large and our calculations support the value obtained by Paulett and Ettinger. Laufer and Okobe also report a heat of formation of 51–60 kcal/mol for diazomethane.¹⁹ This is also surprisingly far from our computed value. Calculations for the D_e of N₂ using the same extrapolation method as used here give an extrapolated value of 226.8 kcal/mol compared to an experimental value of 228.4 kcal/mol.²⁰ As a further check on the computed results, we also computed the energy of $^3\text{CH}_2+\text{N}_2$ with each of the basis sets. The $^3\text{CH}_2$ geometry was taken from the work of Bauschlicher, Langhoff, and Taylor²¹ who carried out a definitive study of the singlet-triplet splitting in CH₂. These results are also given in Tables I(a)–I(c). Here it is

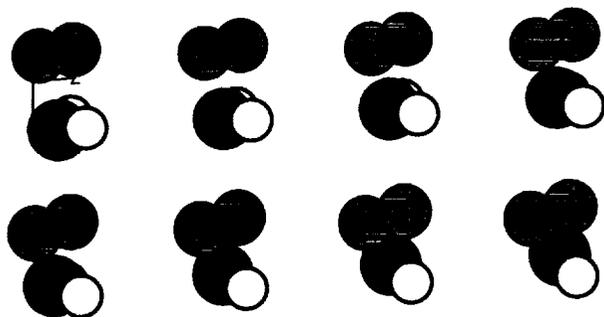


FIG. 4. Geometries along the reaction path connecting $^1\text{CH}_2+\text{N}_2$ with diazirine.

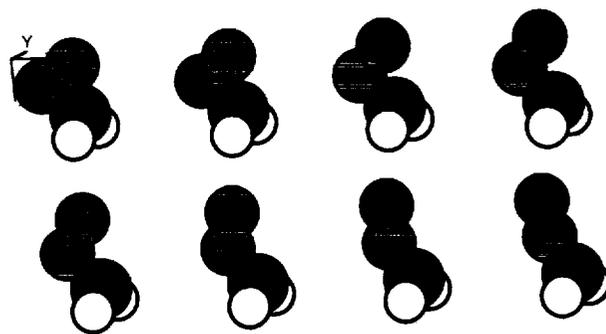


FIG. 5. Geometries along the reaction path connecting diazirine with diazomethane.

seen that the cc-pVQZ basis set gives a separation of 9.7 kcal/mol compared to 9.1 kcal/mol obtained in Ref. 21 with a comparable size ANO basis set. Taking these considerations together leads us to assign a maximum error of 2 kcal/mol to our reported 0 K heats of formation for diazirine and diazomethane.

From Ref. 20 it is expected that the barrier heights obtained with the cc-pVTZ basis set would change by less than 0.5 kcal/mol if extrapolated to the basis set limit. This occurs because the barrier height involves an energy difference between a bond that is being broken and a bond that is forming and therefore there is a cancellation of errors. Accordingly, this extrapolation was not carried out for the barrier heights reported in Table I(b).

Table I(d) gives energetics for the stationary points obtained at the CASSCF level with the pVDZ basis set. As expected, these energetics are much less reliable than those obtained from the ICCI calculations. The general trends are that the binding energies are underestimated and the barrier heights are overestimated. In spite of these obvious defects in the CASSCF energetics, comparison of CASSCF and ICCI stationary points for the N+O₂ reaction²² showed that the CASSCF method does a very good job of predicting the geometry in the directions perpendicular to the reaction coordinate, but that the saddle-point geometries can be shifted somewhat along the direction of the reaction coordinate. An

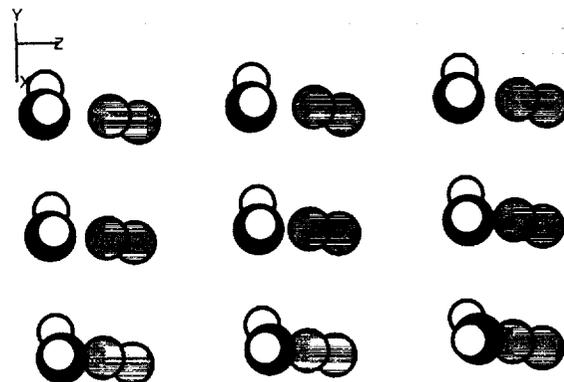
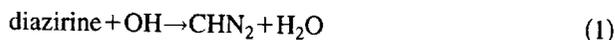


FIG. 6. Geometries along the reaction path connecting $^1\text{CH}_2+\text{N}_2$ with diazomethane.

extreme example of this effect, in the present calculations, occurs for *sp*3, where the ICCI method finds an energy at the saddle-point geometry below that of the reactants. This has been interpreted to mean that the barrier is shifted far out into the entrance channel and in fact there is probably no barrier. In a case where the barrier persists at the ICCI level, the shift along the reaction coordinate is normally much less significant.

We now return to consideration of other product channels in the reaction of ¹CH₂ with N₂. Formation of CH₂N+N is endothermic by 64 kcal/mol and involves a singlet-triplet crossing. Thus, this pathway is not a likely product channel. Dissociation of diazirine to CHN₂+H can lead to either doublet or quartet CHN₂. The quartet state (*q* min 1 of Ref. 1) is 17.0 kcal/mol above the doublet state (*d* min 2). However, CHN₂+H is computed to be endothermic by 66 kcal/mol, with respect to reactants, for the doublet state of CHN₂, and is also not a likely direct product.

More likely processes leading to CHN₂ are hydrogen abstraction from diazirine or diazomethane, both of which are expected to be important products of the reaction of ¹CH₂ with N₂. Hydrogen abstraction from diazomethane leads to an HCN₂ geometry like the dative structure of Manaa and Yarkony.²³ Previous theoretical studies¹ indicate that there is a large barrier between the dative structure and the region of the surface leading to HCN+N. Thus, this pathway is not expected to contribute to prompt NO formation. On the other hand, hydrogen abstraction from diazirine leads to an HCN₂ geometry like that involved in the doublet-quartet surface crossing region of the CH+N₂ surface. For example, the reaction



is exothermic by 28.5 kcal/mol. In addition, assuming no vibrational relaxation, diazirine formed from ¹CH₂+N₂ would have about 38 kcal/mol of internal energy (energy of *sp*₁ minus energy of min 2), leading to a total of 66 kcal/mol of available energy. As the NN bond is considerably shorter in diazirine it is probable that CHN₂ will be formed with a large amount of energy in the NN stretching mode. [The quartet state of CHN₂ has a longer NN bond (2.377 Å) than the doublet state (1.635 Å), which in turn is longer than the NN bond in diazirine (1.253 Å).] From Ref. 1 the saddle points leading to CH+N₂ on the doublet surface and to HCN+N on the quartet surface are 31 kcal/mol and 36 kcal/mol above *d* min 2, respectively. Thus, if this much energy is transferred into vibrational energy, these channels are energetically accessible. Furthermore, energy in the NN stretching mode also favors the doublet to quartet crossing [In Eq. (1) the CHN₂ is formed initially in the doublet state], leading to HCN+N(⁴S), as for the CH(²Π)+N₂ reaction.

V. CONCLUSIONS

The reaction pathways for the reaction of ¹CH₂ with N₂ have been studied using complete active space self-consistent field (CASSCF) derivative methods to characterize the stationary points and internally contacted configuration interaction (ICCI) to determine the energetics.

¹CH₂+N₂ can lead to diazomethane, with no barrier, or to diazirine, with a barrier of 5 kcal/mol. Diazirine is computed to be about 24 kcal/mol below ¹CH₂ plus N₂. Rearrangement to diazomethane involves a 20 kcal/mol barrier, with respect to reactants, and diazomethane is computed to be about 34 kcal/mol below ¹CH₂ plus N₂. The CH₂N+N and CHN₂+H channels are computed to be endothermic by 64 kcal/mol and 66 kcal/mol, respectively. Thus, these product channels are unlikely to be important.

The computed potential energy surface would suggest that diazirine will be readily formed from ¹CH₂ plus N₂. It is proposed that subsequent reaction of diazirine with hydrogen abstractors such as OH, which would be abundant in the combustion environment, would lead to doublet CHN₂, with considerable vibrational excitation, especially in the NN stretch mode, which would facilitate doublet to quartet crossing, leading to HCN+N product. Thus, this pathway may be an important new source of "prompt" NO.

ACKNOWLEDGMENT

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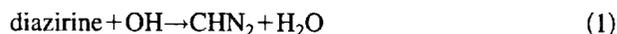
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extreme example of this effect, in the present calculations, occurs for *sp*3, where the ICCI method finds an energy at the saddle-point geometry below that of the reactants. This has been interpreted to mean that the barrier is shifted far out into the entrance channel and in fact there is probably no barrier. In a case where the barrier persists at the ICCI level, the shift along the reaction coordinate is normally much less significant.

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