should be obtained as a product as well. No isocyanide has been reported in the experimental studies[18,19] of the rearrangements of 2*H*-azirine to acetonitrile. Apparently no attempt was made to identify methyl isocyanide, which in any event would be rapidly converted to acetonitrile if the temperature were 650 K or above.[38] There are also possibilities involving bimolecular pathways which we have not considered in this study. Finally, it is of interest that recent experimental studies[39] of the gas-phase thermal isomerization of 3*H*-isoxazoles to α-carbonylacetonitrile derivatives have pointed to 2*H*-azirines as intermediates.

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Registry No. Vinyl nitrene, 64987-66-2; 2*H*-azirine, 157-16-4; methyl isocyanide, 593-75-9; acetonitrile, 75-05-8; ketenimine, 17619-22-6.

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Ab Initio CI Study of Chemical Reactions of Singlet and Triplet NH Radicals

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Abstract: Reactions of the NH radical in its low electronic states ($^3\Sigma^-$, $^1\Delta$, $^1\Sigma^+$, and $^3\Pi$) with hydrogen and ethylene have been investigated by the multireference double-excitation (MRD) CI method employing mainly the 4-31G basis set. The 4-31G** basis set has been utilized for special points of interest. It is confirmed that the relative energies of these low-lying states calculated by this method are in satisfactory agreement with the experimental data. The insertion of NH($^3\Pi$) into H_2 is predicted to proceed maintaining the planar (C_{2v}) symmetric structure with an extremely low-energy barrier. NH($^1\Delta$) inserts into hydrogen and cyclo-adds to ethylene with no barrier at all. The minimum-energy path for the addition of NH($^3\Sigma^-$) to ethylene has been searched for. The activation barrier height is calculated to be not larger than 24 kcal/mol. The CH_2CH_2NH radical has various local energy minima, among which the face-to face (FF) singlet diradical is the most stable. Cyclization of the singlet FF diradical to form the ground-state aziridine has virtually no energy barrier. It has been demonstrated that the singlet and triplet diradical states in the face-to-edge (FE) conformation are correlated with the first excited singlet (S_1) and the lowest triplet (T_1) state of aziridine, respectively. Implications of all these results are discussed in comparing the reactivities of CH_2 and O as isoelectronic homologues of NH.

I. Introduction

The imidogen radical NH is an intriguing chemical species which is isoelectronic with CH_2 and O. Despite an intuitive anticipation of a similarity of its chemical behavior to those of such isoelectronic homologues, its chemistry has hitherto been far less well explored. It has so far only been disclosed experimentally that the first excited singlet NH($^1\Delta$) inserts readily into a paraffin single bond in the gas[1] as well as in the liquid[2] phase, while the ground-state triplet NH($^3\Sigma^-$) can undergo addition toward radical species[3,4] and olefins[5] in the gas phase. The chemical reactivity of NH in its higher lying electronic states is still comparatively unknown. It is felt that systematic investigations of the chemistry of the NH radicals would not only be academically rewarding but practically important, particularly in relation to their possible participation in chemical cycles involved in the upper atmosphere.

Theoretical considerations of the characteristics of NH reactions have also been surprisingly scanty. The only example of such studies is an ab initio SCF treatment of the CH_2CH_2NH diradicals to be formed by the addition of NH($^3\Sigma^-$) to ethylene.[6] Emphasis there has been placed at the stabilities of such diradicals relative to aziridine as the ring-closed product. The results are highly illuminating but insufficient to be used at present as a theoretical guide for the reaction in question.

The present investigation employs ab initio MO configuration-interaction (CI) treatments for description of reactions in which the NH radicals in various low-lying electronic states ($^1\Delta$, $^1\Sigma^+$, $^3\Sigma^-$, and $^3\Pi$) are involved. Molecular hydrogen and ethylene were chosen as prototypes of reaction partners. Search for the minimum-energy paths and characterization of the electronic structures of the reacting systems along reaction paths are the matters of our primary concern. Particular attention has been paid to the diradical character as well as the thermochemical stability of the aforementioned CH_2CH_2NH intermediate. The state correlations of various stable conformations of the CH_2CH_2NH diradicals, both singlet and triplet, with ring-closed aziridine in different electronic states will also be elucidated. The results of these treatments provide an useful qualitative guide for the consideration of the dynamic phase of the NH reactions which

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Table I. NH($^1\Delta$) and NH($^3\Sigma^-$) Calculated with Various Basis Sets

		SCF[b]			CI, $T = 0$			"full" CI[c]
basis set[a]	state	r, Å	f, mdyn/Å	E, hartrees	r, Å	f, mdyn/Å	E, hartrees	E, hartrees
A	$^1\Delta$	1.028	5.86	−54.811 3	1.072	4.38	−54.864 4	−54.865 7
	$^3\Sigma^-$	1.030	6.48	−54.880 5	1.079	4.69	−54.936 8	−54.938 4
	gap[d]			43.4			45.4	45.7
B	$^1\Delta$	1.020	7.04	−54.833 6	1.037	6.11	−54.959 5	−54.964 6
	$^3\Sigma^-$	1.024	7.22	−54.902 1	1.042	6.26	−54.027 1	−55.032 5
	gap[d]			43.0			42.4	42.6
C	$^1\Delta$	1.033	5.83	−54.883 3	1.062	5.30	−54.958 9	−54.961 4
	$^3\Sigma^-$	1.035	5.99	−54.951 3	1.064	5.40	−55.029 7	−54.032 6
	gap[d]			42.7			44.4	44.7
D	$^1\Delta$	1.020	6.76	−54.901 8	1.040	5.68	−55.044 6	−55.051 2
	$^3\Sigma^-$	1.021	6.73	−54.969 1	1.045	5.96	−55.110 0	−55.116 8
	gap[d]			42.2			41.0	41.2
exptl[e]	$^1\Delta$				1.034	5.59		
	$^3\Sigma^-$				1.0362	5.93		
	gap[d]						36.0	

[a] A, 4-31G; B, 4-31G** in which the exponents for one set each of d(N) and p(H) functions are $\alpha_N = 0.913$ and $\alpha_H = 0.75$, respectively; C, (9s5p/4s)/[5s3p/2s]; D, (9s5p2d/4s1p)/[5s3p1d/2s1p] in which the exponents for two sets of d(N) functions are $\alpha_1 = 1.8846$ and $\alpha_2 = 0.5582$ with the coefficients $d_1 = 0.35785$ and $d_2 = 0.75961$, and the exponent for a set of p(H) functions is $\alpha = 0.735824$. [b] Open-shell singlet SCF procedure is used for $^1\Delta$. [c] Estimated at the respective bond distance r corresponding to the CI, $T = 0$ energy minimum. [d] The total energy in kcal/mol of NH($^1\Delta$) relative to NH($^3\Sigma^-$). [e] Reference 12.

has to be treated on a more quantitative basis.

II. Method of Calculation

All calculations were carried out employing the multireference double-excitation (MRD) CI method.[7] The open-shell formalism of Roothaan's restricted Hartree–Fock (HF) SCF MO theory[8] was utilized for generating one-electron wave functions for the triplet state of a given molecular system, whether it is an isolated entity or a molecular aggregate. In the case of an open-shell singlet state as for singlet diradicals, the same open-shell procedure was used for HF singlet states if two singly occupied MO's belong to two different irreducible representations of the molecular point group. For the singlet states for which this requirement is not satisfied and the closed-shell SCF is inadequate, the triplet SCF MO's were employed as one-electron functions for building up the singlet CI spaces. It has been shown in a number of papers[9] that the one-electron functions obtained from the triplet SCF procedure based on the electronic configuration with two singly occupied MO's (HOMO and LUMO) yield a balanced description of both radical centers which is not the case in the closed-shell singlet SCF procedure. The unbalanced description of radical centers cannot always be corrected by large-scale but incomplete CI treatments.

Selection of configurations obtained by single and double excitations with respect to the reference configurations was carried out according to the energy selection criterion set by the chosen selection threshold T. The lowest selection threshold T used in this work is either $T = 0$ (full single and double CI with respect to reference configurations) or $T = 10$ μhartrees, depending on the dimension of the CI space encountered. In the latter case, the extrapolation technique has been employed for calculating energies at the limit $T \rightarrow 0$. In either case, Davidson's perturbational estimate of the full CI energies has been made.

The atomic orbital basis sets used in the most part of the present work are the standard split-valence 4-31G basis functions.[10a] Polarization functions for the carbon and nitrogen atoms as well as for the hydrogen atom were included, whenever it was considered to be appropriate. For example, the 4-31G** basis set has been frequently employed for which the exponents of one set of d functions at the carbon atom and at the nitrogen atoom and of one set of p functions at the hydrogen atom have been taken from the 6-31G** basis set designed for the treatment of the molecular ground-state correlated wave functions.[10b] Less contracted larger basis sets[11] with and without the polarization functions were also employed for the comparative studies of the lowest lying singlet ($^1\Delta$) and triplet ($^3\Sigma^-$) states of NH itself.

III. Low-Lying Electronic States of NH

Prior to the investigations of reactions, we will briefly consider the structure and relative energies of the NH radical in some low-lying electronic states. The aim of this section is to examine the dependence of the energy gap between the lowest triplet and singlet states as well as the dependence of the excitation energies of other low-lying states on the choice of the AO basis sets and one-electron functions employed in the CI treatments. Such preparatory studies will be a particularly meaningful digression here, even though the primary concern of the present work is to discuss the features of reactions involving several low-lying singlet and triplet NH states, which we intend to do in a comparative manner rather than separately.

Firstly, we have located the SCF as well as the CI energy minima for the lowest singlet ($^1\Delta$) and triplet ($^3\Sigma^-$) states. The characteristic leading configurations of these lowest lying NH states are as follows:

$^1\Delta$: (a) closed-shell representation

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2[(\pi_x)^2 - (\pi_y)^2] \text{ abbreviated as } [(\pi_x)^2 - (\pi_y)^2]$$

$^1\Delta$: (b) open-shell representation

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(\pi_x)(\pi_y), \text{ abbreviated as } [(\pi_x)(\pi_y)]_S$$

$$^3\Sigma^-: \quad (1\sigma)^2(2\sigma)^2(3\sigma)^2(\pi_x)(\pi_y), \text{ abbreviated as } [(\pi_x)(\pi_y)]_T$$

It is obvious that the closed-shell SCF procedure yields only one component of the $^1\Delta$ state.

The atomic-orbital basis sets selected for use in computations are: set A, the conventional split-valence 4-31G functions;[10a] set B, the 4-31G** which is an augmentation of the 4-31G by the one set of d functions on the N atom and by one set of p functions on the H atom;[10b] set C, the standard contracted double-ζ functions[11] which are represented conventionally by the notation

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Table II. Low-Lying Electronic States of NH at the Experimental Bond Distances[a]

state	r, Å	relative energies, kcal/mol				dipole moment, D	main configurations
		SCF	CI, $T = 0$[b]	"full" CI	exptl		
$^3\Pi$	1.037	86.5	86.2 (309)	86.4	85.2	1.486	$0.974(3\sigma)(\pi_x)$
$^1\Sigma^+$	1.036		63.8 (113)	62.7	60.6	1.682	$0.467(\pi_x)^2$ $0.467(\pi_y)^2$ $0.017(1\sigma)^2(2\sigma)^2(\pi_x)^2(\pi_y)^2$ $0.013(1\sigma)^2(3\sigma)^2(\pi_x)^2(\pi_y)^2$
$^1\Delta$	1.034	43.4[c]	45.2 (113)	45.4	36.0	1.807	$0.489(\pi_x)^2$ $0.489(\pi_y)^2$
$^3\Sigma^-$	1.036	0[d]	0[d] (138)	0[d]	0	1.801	$0.974(\pi_x)(\pi_y)$

[a] The basis set used is 4-31G. [b] Figures given in parentheses indicate the dimension of the CI space. [c] Open- shell singlet SCF procedure is used. [d] The SCF, CI, $T = 0$ and "full" CI energies for the $^3\Sigma^-$ as the standard are −54.88042, −54.93571, and −54.93720 hartrees, respectively.

(9s5p/4s)/[5s3p/2s]; and set D, the double-ζ basis C augmented by the polarization functions[11] (9s5p2d/4s1p)/[5s3p1d/2s1p].

The results of calculations are summarized in Table I. The open-shell SCF procedure has been employed for the treatment of $^1\Delta$ state. It is apparent from this table that the N–H bond distances r at the SCF energy minima are smaller than the experimental values independent on the AO basis set chosen. In contrast, those obtained by the CI, $T = 0$ calculations are somewhat too large. Inclusion of the polarization functions (sets B and D) shows an obvious trend of diminishing the equilibrium bond distance. With any of the basis sets employed, the optimal r value is predicted to be slightly greater for $^3\Sigma^-$ than for $^1\Delta$, in agreement with experiment.[12]

The calculated energy gap between the two states is too large in comparison with the experimental value of 36 kcal/mol.[12] It is worth mentioning that the energy gap is not improved by the CI procedure unless polarization functions are included in the AO basis sets (sets B and D). The force constants f for the N–H bond stretching are also improved accordingly; the f values calculated by use of the set D are in almost perfect agreement with the experimental data.

The energy gap between $^1\Delta$ and $^3\Sigma^-$ has already been a subject of theoretical investigation by previous workers. Thus, Kuba and Öhrn[13] first reported the results of CI calculations indicating an energy gap of 43.8 kcal/mol. The predicted equilibrium bond lengths were 1.12 Å ($^1\Delta$) and 1.13 Å ($^3\Sigma^-$). O'Neil and Schaefer[14] obtained a similar CI energy gap of 46.1 kcal/mol at the improved bond distances of 1.037 Å ($^1\Delta$) and 1.041 Å ($^3\Sigma^-$). So far, the most extensive SCF calculations reported by Huo[15] make use of the basis set involving d and f functions for N and p functions for H. They obtained the energy gap of 42.1 kcal/mol. Our CI, $T = 0$ treatment as well as the "full" CI estimate with the basis set D provides an improvement of only 1 kcal/mol over their result, showing a trend toward the agreement with the experimental result.

The $^1\Sigma^+$ and $^3\Pi$ states of NH are higher lying than the $^1\Delta$ state. These two excited states conform to the following representations:

$$^1\Sigma^+\!: (1\sigma)^2(2\sigma)^2(3\sigma)^2[(\pi_x)^2 + (\pi_y)^2], \quad \text{abbreviated as } [(\pi_x)^2 + (\pi_y)^2]$$

$$^3\Pi\!: (1\sigma)^2(2\sigma)^2(3\sigma)(\pi_x)(\pi_y)^2, \text{ abbreviated as} (3\sigma)(\pi_x)$$

The four-reference, two-root (4M/2R) CI treatment has been employed to obtain both singlet states $^1\Delta$ and $^1\Sigma^+$ which can be characterized by negative and positive linear combinations of two electronic configurations $(\pi_x)^2$ and $(\pi_y)^2$, respectively, with equal contributions to the correlated wave functions. The energies of the $^1\Sigma^+$ and $^3\Pi$ states relative to the $^3\Sigma^-$ obtained from the CI treatments employing the 4-31G AO basis are in good agreement with the experimental values. In the case of $^3\Pi$, the two-reference, one-root treatment (2M/1R) is most appropriate. Table II compares the energies, the weights of reference configurations, and the dipole moments for the four electronic states calculated at the experimental bond distances.

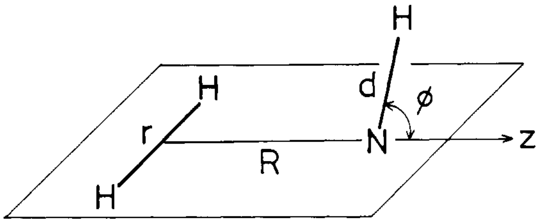

Figure 1. Internal coordinates for the insertion (C_s) of NH into H_2.

It is worth mentioning that the energies of the $^1\Delta$ and $^1\Sigma^+$ states of NH obtained by the described CI treatments are not very sensitive with respect to the choice of the one-electron functions. The triplet SCF MO's and the open-shell singlet SCF MO's which treate the π_x and π_y orbitals in a balanced manner when employed to build up the singlet CI spaces yield almost the same energies for these states.

In summary, the relative energies of low-lying electronic states of NH can be obtained adequately by the MRD-CI procedure at the level of sophistication as adopted here. Quantitatively, however, the calculated energy gap between the $^1\Delta$ and $^3\Sigma^-$ states is still 5–10 kcal/mol too large. No further attempt has been made in this paper to reach the best quantitative prediction of the energy gap. With this reservation in mind, one can proceed to consider chemistry of the NH radicals. Use of the conventional 4-31G basis set, or more preferrably its extension with polarization functions (4-31G**), will suffice for this purpose. Therefore, the 4-31G basis set has been employed for overall investigation while the important points have been recalculated using the 4-31G** basis set.

IV. Reactions with Hydrogen

Molecular hydrogen is chosen here as the simplest prototype of reactant with the NH radical. The reactions considered are the insertions of NH($^1\Delta$, $^3\Sigma^-$, $^3\Pi$) and the abstraction of a hydrogen atom by NH($^3\Sigma^-$). Both the 4-31 G and 4-31G** basis sets have been employed.

A. Insertion Reaction. The minimum-energy path for the insertion of NH into H_2

$$NH + H_2 \rightarrow NH_3 \tag{1}$$

is intuitively expected to be a process maintaining C_s symmetry whether it is thermochemically favorable or not as illustrated in Figure 1. In following the reaction patth, we have chosen the distance R between the N atom and the midpoint of H_2 as the primary reaction coordinate. At given distances R, the geometry of the entire system has been first SCF optimized with respect to all the rest of internal coordinates d, r, and ϕ. The CI treatments with the energy selection threshold $T = 10$ μhartrees have been employed for the optimized geometries. The entire system has been forced to maintain either C_s symmetry ($\phi \neq 0°$) or C_{2v} symmetry (in case where the optimized geometry conforms

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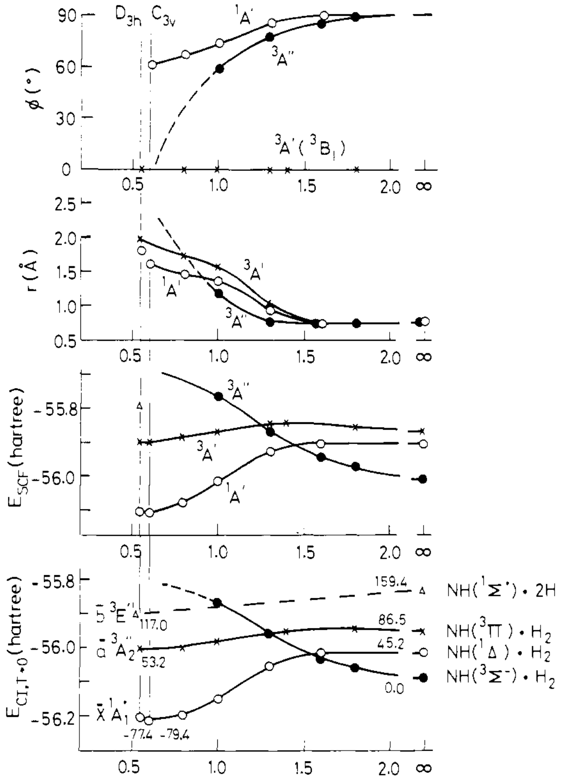

Figure 2. Variations in geometry and energy as the functions of the intermolecular distance R for the insertions of NH into H_2. The energies $E_{CI,T\to0}$ in kcal/mol appended to the plotted points are relative to the isolated NH($^3\Sigma^-$) + H_2 system as the reference point. The 4-31G AO basis set has been employed.

to $\phi = 0°$) during the course of reaction.

In Figure 2 are shown the varitions in the 4-31G SCF optimized ϕ and r as well as the energies (E_{SCF} and $E_{CI,T\to0}$) as functions of R for the insertion processes of NH($^1\Delta$), NH$^3\Pi$), and NH($^3\Sigma^-$).

The insertion of NH($^1\Delta$) is regarded as a typical example of orbital-symmetry-allowed processes.[16] E_{SCF} as well as $E_{CI,T\to0}$ decreases continuously as R decreases, until the reacting system reaches NH_3 in its ground electronic state ($\tilde{X}^1A_1$). The angle ϕ, which is initially 90° at the separation R greater than 1.8 Å, decreases also continuously down to 61.1°. The H–H interatomic distance r continues to increase accordingly, and the electronic structure of the entire system remains in the irreducible representation $A'(C_s)$ throughout the course of reaction. The NH_3 formed is pyramidal (C_{3v}) in structure with the NH bond distance 0.991 Å and the HNH bond angle 115.9°. The corresponding experimental values are 1.012 Å and 106.7°, respectively.

Separate calculations have shown that the NH_3 molecule, when forced to take the planar structure (D_{3h}), has the optimal N–H bond distance reduced to 0.982 Å. The planar NH_3 has been found to be ca. 2.0 kcal/mol less stable than the pyramidal form in the CI treatments (comparison is made for extrapolated energies ($T \to 0$)). The result is to be compared with the experimental inversion barrier height of 5.8 kcal/mol.[17] The energy change for this insertion process is calculated to be $\Delta E = -124.6$ kcal/mol, in fair agreement with the experimental heat of reaction $\Delta H°_0 = -131 \pm 3$ kcal/mol.[18,19]

The insertion of NH($^3\Pi$) is chemically interesting. Calculations indicate that the minimum-energy path for the NH($^3\Pi$) insertion is such that the N–H bond continues to lie on the H_2–N plane ($\phi = 0°$) all the way from the outset of reaction to the completion of insertion. The electronic structure of the entire reaction system continues to belong to the irreducible representation $B_1(C_{2v})$ and hence to $A'(C_s)$. Thus, one of the two unpaired electrons is accommodated in the nitrogen p_x orbital perpendicular to the molecular plane while the other occupies the nitrogen sp hybrid orbital oriented toward H_2. The barrier height which is necessary to overcome for a completion of the reaction is only 2.6 kcal/mol at $R \sim 1.8$ Å. The reactant system eventually reaches the lowest triplet state of NH_3

$$\tilde{a}^3A_2''(D_{3h}):\ (1a_1')^2(2a_1')^2(1e')^4(1a_2'')\ (3a_1')$$

which is planar in structure. The odd electron originally present in the p_x orbital of the N atom remains as such ($1a_2''$) in the triplet state of the formed NH_3. On the other hand, the singly occupied sp hybrid orbital overlaps with the H_2 bonding orbital to give one of the $1e'$ orbitals, on one hand, and the $3a_1'$ orbital, on the other. The reaction is thus considered to be a fairly "smooth" process in many respects. The calculated energy change for reaction is $\Delta E = -33.3$ kcal/mol.

Unlike the reactions of NH($^1\Delta$) and NH($^3\Pi$), the insertion of NH($^3\Sigma^-$) costs a great deal of potential energy. If the entire reacting system is forced to maintain the C_s symmetry, its electronic structure should continue to belong to the irreducible representation $A''(C_s)$. The N–H inclination angle decreases from 90° toward 0° monotonically. The energy of this A'' system continues to increase as R decreases. It crosses the NH($^3\Pi$)–H_2 curve at $R = 1.30$ Å. The calculated potential-energy height of this crossing point is 82.1 kcal/mol relative to the isolated NH($^3\Sigma^-$) + H_2. In order that the insertion of NH($^3\Sigma^-$) into H_2 gives the lowest triplet $NH_3(\tilde{a}^3A_2'')$, the electronic state of the four-atomic system has to switch from the irreducible representation $A''(C_s)$ to $A'(C_s)$. At the same time, its spatial structure needs to be changed abruptly from a pyramidal to a planar form in the vicinity of the crossing point. The insertion of NH($^3\Sigma^-$) to H_2 to give a triplet NH_3 is thus a highly unfavorable orbital-symmetry forbidden process.

Symmetry considerations show that the second excited triplet $NH_3(\tilde{b}^3E'')$ in the planar (D_{3h}) system seems to be correlated with NH($^1\Sigma^+$) + 2H(^{2}S) by retaining the $A''(C_s)$ structure. Since the latter correlation was not checked by calculations, it has been shown only tentatively with a broken line in Figure 2.

Similar SCF geometry optimizations have been performed with the 4-31G** basis set for all three types of insertion processes. CI treatments employing the 4-31G** basis set have been carried out for both the 4-31G and 4-31G** optimized geometries. These additional calculations confirmed that the essential features of these processes remained unchanged. However, quantitative aspects of reactions such as the product structure and the heat of reaction do appear to be influenced by the use of polarization functions. In Table III, such data of interest which have been obtained with the different basis sets are compared in particular for the insertion of NH($^1\Delta$). The CI calculations with the 4-31G** basis set for the SCF optimized geometries in the same basis yield the most reliable results. For instance, the N–H bond distance and the HNH bond angle of $NH_3(\tilde{X}^1A_1)$, optimized geometries in the same basis yield the most reliable results. For instance, the N–H bond distance and the HNH bond angle of $NH_3(\tilde{X}^1A_1)$, optimized with the 4-31G** SCF procedure are 1.0 Å and 107.4°, respectively, which are in better agreement with the experimental data. The inversion barrier height of 8.5 kcal/mol and the energy change of reaction $E = -128.6$ kcal/mol, both in the CI, $T \to 0$ limit, are also significant improvements over the aforementioned 4-31G results.

B. Hydrogen Abstraction by NH($^3\Sigma^-$). Occurrence of the abstraction of a hydrogen atom from molecular hydrogen by NH($^3\Sigma^-$)

$$NH(^3\Sigma^-) + H_2 \to NH_2 + H \qquad (2)$$

has not yet been confirmed experimentally, despite its similarity in type with the familiar reaction O(^{3}P) + H_2 → OH + H. Probably the reaction is inherently a high activation-energy process

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(16) Woodward, R. B.; Hoffmann, R. "The Concervation of Orbital Symmetry"; Academic Press: New York, 1970.

(17) Rauk, A.; Allen, L. C.; Clementi, E. *J. Chem. Phys.* **1970**, *52*, 4433.

(18) Calculated on the basis of the experimental heat of formation, $\Delta H_0° = 3.65 \pm 0.10$ eV, for NH($^3\Sigma^-$): Piper, L. G. *J. Chem. Phys.* **1980**, *72*, 1303.

(19) The heat of reaction was calculated from the relevant data for the heats of formation: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

Table III. Energy Changes Accompanying the Insertion Reaction $NH(^1\Delta) + H_2 \rightarrow NH_3(X^1A_1)$

geometry optimization	CI	energy	ΔE_{inv},^{a} kcal/mol	ΔE^b kcal/mol $NH_3(C_{3v})$	E, hartree $NH_2 + H$
4-31G	4-31G	SCF	0.5	−105.8	−55.938 1
		CI, $T \rightarrow 0$	2.0	−124.6	−55.013 4
		"full" CI	2.2	−125.4	−55.016 1
4-31G	4-31G**	SCF	3.2	−108.6	−55.964 8
		CI, $T \rightarrow 0$	4.5	−124.6	−56.126 1
		"full" CI	4.7	−127.1	−56.131 7
4-31G**	4-31G**	SCF	6.1	−111.6	−55.964 7
		CI, $T \rightarrow 0$	8.5	−128.6	−56.126 0
		"full" CI	8.8	−131.5	−56.131 6
exptl			5.8^c	−131 ± 3^d	

[a] Inversion barrier height, $\Delta E_{inv} = E(D_{3h}) - E(C_{3v})$. [b] Energy changes, $\Delta E = E(C_{3v}) - E(NH_2 + H)$. [c] Reference 17. [d] References 18 and 19.

Table IV. Barrier Heights, $\Delta E^{\ddagger}$, and the Energy Change, ΔE, for the Abstraction Reaction $NH(^3\Sigma^-) + H_2 \rightarrow NH_2(\tilde{X}^2B_1) + H$

geometry optimization	CI	energy	$\Delta E^{\ddagger}$, kcal/mol TS	ΔE, kcal/mol $NH_2 + H$	E, hartree $NH(^1\Delta) + H_2$
4-31G	4-31G	SCF	44.2	22.8	−56.007 3
		CI, $T \rightarrow 0$	28.6	20.1	−56.086 8
		"full" CI	24.3	19.2	−56.088 5
4-31G	4-31G**	SCF	39.6	17.9	−56.033 4
		CI, $T \rightarrow 0$	28.3	18.4	−56.193 7
		"full" CI	24.3	17.0	−56.199 5
4-31G**	4-31G**	SCF	40.3	17.5	−56.033 4
		CI, $T \rightarrow 0$	27.1	17.8	−56.193 6
		"full" CI	23.6	16.4	−56.199 3

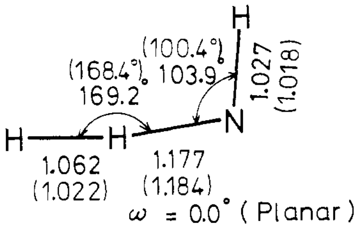


Figure 3. Transition-state geometry for the reaction $NH(^3\Sigma^-) + H_2 \rightarrow NH_2 + H$. Bond distances are given in Å. The values given in parentheses are those obtained by the 4-31G** SCF optimization.

which will not permit observations under usual experimental conditions.

Figure 3 shows the geometry of the transition state located by the SCF procedure employing the 4-31G and the 4-31G** AO basis set. All the atoms lie on a single plane, and the terminal H–H and N–H bonds are in s-cis position to each other exactly as in the case of the reaction $OH(^2\Pi) + H_2 \rightarrow H_2O + H$.[20]

The barrier heights, $\Delta E^{\ddagger}$, for the transition-state (TS) geometries and the energy changes, ΔE, for reaction have been calculated with both 4-31G and 4-31G** basis sets. The results are summarized in Table IV. The calculated SCF barriers for the 4-31G TS geometry with and without polarization functions are 44.2 and 39.6 kcal/mol, respectively. The SCF energy lowering due to the inclusion of polarization functions is thus ca. 5 kcal/mol. The CI, $T \rightarrow 0$ treatment lowers these barrier energies to the values of 28.6 and 28.3 kcal/mol, respectively. The estimated "full" CI values coincide with each other (24.3 kcal/mol). The 4-31G** CI treatment of the 4-31G** TS geometry further lowers $\Delta E^{\ddagger}$. The CI, $T \rightarrow 0$ and the "full" CI values are 27.1 and 23.6 kcal/mol, respectively. The activation energy for this abstraction reaction, obtained with the CI treatment at the present level of sophisticaion, is not smaller than 24 kcal/mol, even when the vibrational zero-point energy is taken into account.

The 4-31G** CI procedure tends to give lower values for the energy change, ΔE, than the 4-31G CI treatment. The effect of geometry is almost without importance here. The lowest value for ΔE obtained in this work is 16.4 kcal/mol (the 4-31G** "full" CI result for the 4-31G** SCF optimal geometry). It is still too large as compared with the experimental heat of reaction $\Delta H° = 9.9 \pm 3$ kcal/mol.[18,19]

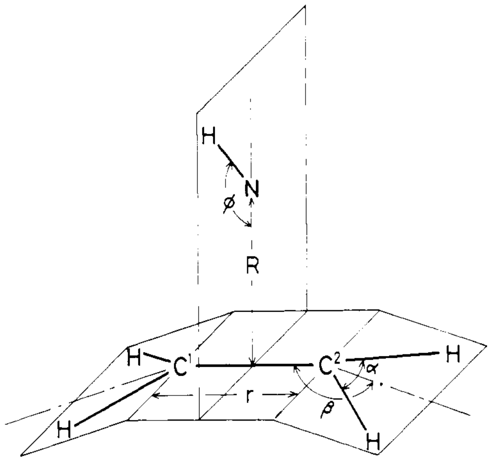
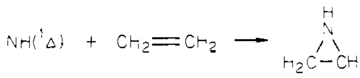


Figure 4. Internal coordinates used for the cycloaddition of $NH(^1\Delta)$ to C_2H_4.

V. Reactions with Ethylene.

In this section, the energetics of the reactions of NH with ethylene will be investigated. The reactions considered are of two types: one is the concerted cycloaddition of $NH(^1\Delta)$ yielding aziridine; the other is the addition of $NH(^3\Sigma^-)$ to one of the ethylene carbon atoms, giving rise to a triplet diradical, CH_2CH_2NH.

A. Cycloaddition of $NH(^1\Delta)$. The cycloaddition of $NH(^1\Delta)$ toward ethylene is an orbital-symmetry-allowed process



$$NH(^1\Delta) + CH_2{=}CH_2 \longrightarrow \text{aziridine } (H\text{–}N<, H_2C\text{–}CH_2) \qquad (3)$$

No doubt, the $NH(^1\Delta)$ radical will approach ethylene along the symmetric least motion path where the ethylene carbon atoms and NH retain a local C_s symmetry (Figure 4).

An approximate experimental geometry of aziridine is available in the literature.[21] According to the reported geometry, the

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[20] Walch, S. P.; Dunning, T. H., Jr. *J. Chem. Phys.* **1980**, *72*, 1303.

Table V. Energy Changes for the Concerted Cycloaddition of NH($^1\Delta$) to Ethylene

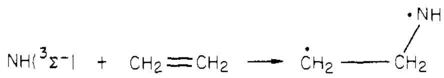
	path point, R (Å) =			
	1.291	1.70	2.00	∞[a]
assumed geometry				
r (Å)	1.480	1.405	1.354	1.330
β (deg)	159.4	169.7	174.9	180
ϕ (deg)	112.0	100.2	93.3	
relative energies (kcal/mol)[b]				
SCF	−54.5	−20.4	1.5	0
CI, T → 0	−77.3	−48.3	−15.0	0
"full" CI	−82.9	−56.5	−21.8	0
weight of main configuration	0.908	0.895	0.896	0.910

[a] The SCF, CI, $T \to 0$, and "full" CI energies at $R = \infty$ as standard are −132.7331, −132.9598, and −132.9751 hartrees, respectively. [b] All the CI energies were obtained from the variational one-reference, one-root (1M/1R) treatment with the selection threshold $T = 10$ μhartrees.

deformation of the ethylenic moiety is such than only r (=1.480 Å) and δ (=159.4°) difer appreciably from the corresponding values for an isolated ethylene. Therefore, in this work we have decided to follow the least motion path by adjusting only r and β in addition to the N–H inclination angle ϕ. The other geometry parameters were fixed at the values known for the reactant NH($^1\Delta$) and ethylene.

The results of calculation are given in Table V. The SCF energy minimum located by the partial optimization of the geometry is lowered monotonically as the intermolecular distance R decreases. At the final stage of reaction, where R = 1.291 Å for the experimental geometry, the total SCF energy is lowered by 54.5 kcal/mol in comparison with the energies of the separated reactants. The CI procedure applied at the SCF optimized geometries does not alter overall picture; the potential energy curve is nearly parallel, shifted downward beneath the SCF curve. The estimated full CI energy lowering by reaction is ~80 kcal/mol. The calculated heat of reaction is too small in magnitude as compared with $\Delta H° = -103.2$ kcal/mol.[19] No attempt has been made to minimize the energy along the reaction path in this AO basis or to enlarge the basis set in order to improve the result for the heat of reaction. Nevertheless, these calculations are sufficient to demonstrate qualitatively the inherent case of this symmetry-allowed reaction. The weight of the closed-shell ground configuration in the CI expansion is invariantly as large as ca. 90% throughout the course of reaction. This last point is also in the line with the obvious allowed concerted character of the reaction.

B. Addition of NH($^3\Sigma^-$). In formal analogy to the reaction of O(^{3}P) toward ethylene,[22] the NH($^3\Sigma^-$) is expected to be capable of adding to one of the carbon atoms of ethylene to give the ethylenimine diradical: In fact, there exist several lines of evidence which suggest that reaction 4 represents the primary step of the NH($^3\Sigma^-$) ethylene reaction.[5] Here, we wish to unravel characteristics of this elementary reaction theoretically.



$$NH(^3\Sigma^-) + CH_2{=}CH_2 \longrightarrow \dot{C}H_2{-}CH_2{-}\dot{N}H$$

(4)

To begin with, location of the triplet SCF energy minimum for the CH_2CH_2NH diradical (hereafter being abbreviated as CCN) was undertaken. It is assumed that CCN has a molecular symmetry of the point group C_s. Also, since we are interested in the structure of CCN to be formed directly by reaction 4, we ignore the rotation of the terminal CH_2 group. The internal coordinates necessary to characterize such a geometry are shown in Figure 5. The geometry of our interest at this moment is thus the face-to-edge (FE) conformation[23] (cf. also Figure 7).

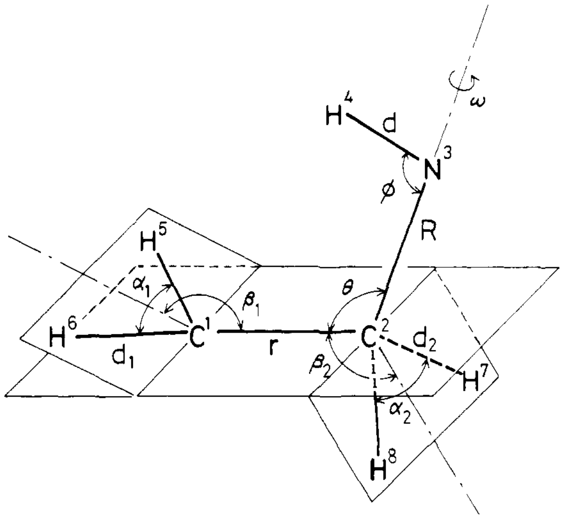


Figure 5. Internal coordinates for the CH_2CH_2NH system (C_s).

Full geometry optimization of triplet CCN in its FE conformation has been carried out employing the unrestricted Hartree–Fock (UHF) SCF method combined with the energy gradient technique. In making an initial guess of the geometry, the optimized structure reported for a similar conformation of the triplet CH_2CH_2O diradical was utilized.[24] Only the length d and the angle ϕ of the N–H bond had to be newly guessed. The full geometry optimization yields two SCF energy minima. One is a structure having the N–H bond s-cis (ω = 0°) to the C–C bond, whereas the other has the N–H bond in the s-trans (ω = 180°) orientation. The former orientation (^3FE_c) has been calculated to be more stable by a negligible amount of 0.3 kcal/mol than the latter (^3FE_t).

Next, the transition states for both the NH($^3\Sigma^-$) additions giving the ^3FE_c and ^3FE_t diradicals have been searched for by successively elongating the C–N bond distance R. At given lengths R, the geometries have been optimized with respect to all the remaining internal coordinates. At the located saddle point, the C–N bond has been found to be elongated by ca. 0.39 Å. The UHF SCF energy is lower (by ca. 3.4 kcal/mol) for the s-cis than for the s-trans structure. The energy barriers for the two channels of addition are 13.7 and 17.1 kcal/mol, respectively. The optimized transition-state (TS) geometry for the more favorable s-cis case is illustrated in Figure 6, together with the equilibrium (EQ) geometry for the product ^3FE_c diradical.

Finally, one-reference, one-root (1M/1R) CI calculations have been carried out for the transition states as well as for the product CCN diradicals at the respective UHF SCF geometries in both s-cis and s-trans orientations. The dimensions of the CI spaces at the configuration selection threshold T = 10 μhartrees are around 5500. For the sake of comparison, similar calculations have been carried out with the 4-31G**. The results are summarized in Table VI, where the SCF, CI, $T \to 0$, and "full" CI energies are given relative to the corresponding energies for the separated NH($^3\Sigma^-$) + C_2H_4 system.

The data given in Table VI illustrate several interesting points.

(1) The barrier heights calculated for the s-cis channel of reaction are lower than those for the s-trans channel, in the UHF RHF and CI treatments employing the 4-31G basis set. The CI procedure with 4-31G** basis set favors slightly the s-trans over the s-cis transition state.

(2) The CI procedure tends to lower the calculated barrier heights. Nevertheless, the lowering due to the inclusion of cor-

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(21) Turner, T. E.; Fiora, V. C.; Kendrick, W. M. *J. Chem. Phys.* **1955**, *23*, 1966.

(22) (a) Cvetanovič, R. *Adv. Photochem.* **1963**, *1*, 115. (b) Cvetanovič, R. *J. Phys. Chem.* **1970**, *74*, 2730.

(23) The sp^2-type lone-pair orbital lies on the $C^2N^3H^4$ plane and is headed away from H^4. It is implicitly assumed that the sp^2 lone-pair structure is more stable than the structure in which a pair of electrons occupies the nitrogen pπ orbital, leaving the sp^2 hybrid orbital singly occupied. This is indeed the case with the s-cis conformation of singlet as well as triplet HNOO: Yamaguchi, K.; Yabushita, S.; Fueno, T. *J. Chem. Phys.* **1979**, *71*, 2321.

(24) Yamaguchi, K.; Yabushita, K.; Fueno, T.; Kato, S.; Morokuma, K. *Chem. Phys. Lett.* **1980**, *70*, 27.

Table VI. Barrier Heights and Energy Changes for the Addition of NH($^3\Sigma^-$) toward Ethylene Yielding the Triplet FE-Type CH_2CH_2NH Diradicals[5]

		E (kcal/mol)				
		transition state		product diradical		E (hartrees)
method	energy	^3FE_c (ω = 0)	^3FE_t (ω = 180°)	^3FE_c (ω = 0)	^3FE_t (ω = 180°)	NH($^3\Sigma^-$)^a + C_2H_4
4-31G	SCF	29.2	32.8	6.3	5.8	-132.8023
	CI, $T \rightarrow 0^b$	17.0	20.7	2.1	2.9	-133.0320
	"full" CI	11.8	15.5	0.9	2.0	-133.0477
4-31G**	SCF	27.5	30.5	-1.8	-2.6	-132.8615
	CI, $T \rightarrow 0^b$	29.3	28.1	3.6	4.5	-133.2627
	"full" CI	23.6	21.5	2.8	3.8	-133.2936
UHF 4-31G	SCF	13.7	17.1	4.0	4.3	-132.8068^c

[a] The SCF, CI, $T \rightarrow 0$, and "full" CI energies for NH($^3\Sigma^-$) employing the 4-31G basis set are given in footnote *d* of Table II. With the 4-31G** basis set, these energies are -54.9017, -55.0266, and -55.0318 hartrees, respectively. The exponents for d functions on carbon and nitrogen atom are $\alpha_C = 0.626$ and $\alpha_N = 0.913$, and the exponent for p functions on hydrogen atom is $\alpha_H = 0.75$. [b] All the CI energies were obtained from the one-reference, one-root (1M/1R) treatment with the selection threshold $T = 10$. [c] The UHF SCF calculations of NH($^3\Sigma^-$) gives the energy minimum of -55.88495 hartrees at the bond distance 1.032 Å.

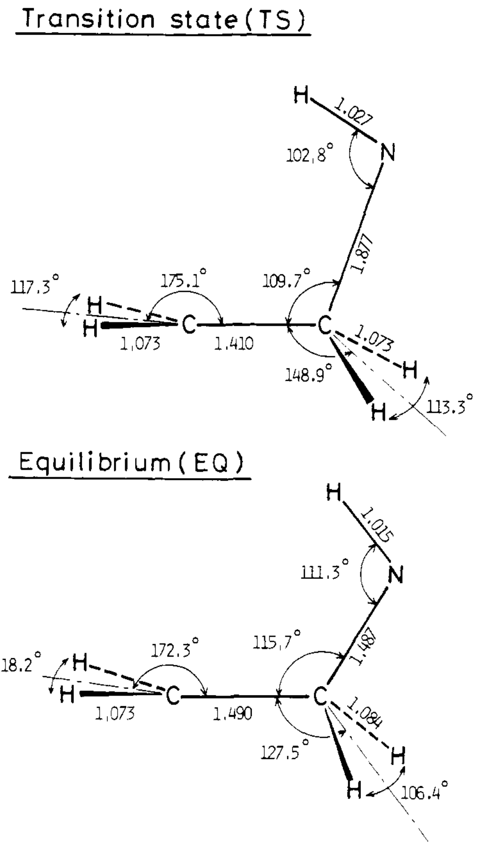

Figure 6. Optimized equilibrium (EQ) and transition-state (TS) geometries for the ^3FE_c C_2H_4–NH system. Bond distances are given in Å.

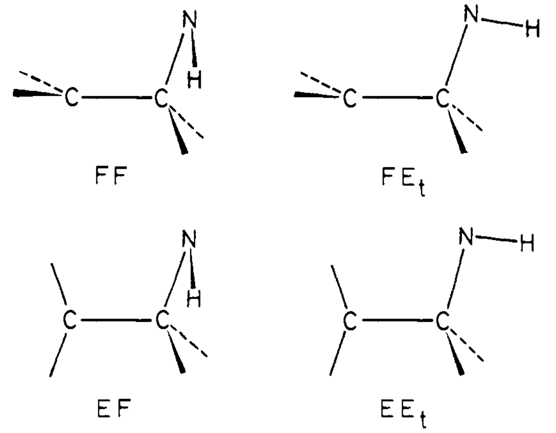

Figure 7. Various conformations for the singlet CH_2CH_2NH diradical.

relation effects is substantially larger for the 4-31G basis set. Moreover, the CI procedure employing the 4-31G** basis set yields a small difference between barrier heights for s-cis and s-trans transition states.

(3) The s-cis and s-trans conformations of the product diradical lie energetically very close to each other (within 1 kcal/mol), and their relative stabilities cannot be concluded in any decisive manner. The RHF SCF procedure employing the 4-31G or 4-31G** basis set predicts ^3FE_t to be slightly more stable than ^3FE_c. The situation is reversed, however, upon inclusion of correlation effects by UHF or the CI procedure.

(4) The CI calculations with both basis sets predict the product diradicals to be slightly less stable as compared with the initial reactant system.

The CI results suggest that the addition is likely to proceed via the s-cis-type transition state with the barrier height which is not larger than ~24 kcal/mol. It should be noted in this connection that both the transition state and the product diradicals are stabilized considerably by an inclusion of polarization functions also in the UHF SCF calculations as will be reported separately.[25] Determination of the stability of the product diradical and of the barrier for the transition states within 5 kcal/mol goes over the scope of the present work.

VI. CH_2CH_2NH Diradicals

The triplet FE CCN diradical, if formed by reaction 4, is likely to undergo isomerization. One conceivable course of isomerization is its cyclization to form aziridine necessarily via an intersystem crossing to a singlet diradical state.[5,22] Considerations of the structures and stabilities of possible diradical states, both singlet and triplet, may well benefit the understanding of the chemistry of the CCN diradical.

A. Various Diradical States. As has already been mentioned, the triplet CCN diradical has energy minima at the FE_c (ω = 0°) and at FE_t (ω = 180°) conformations. In other words, the rotation of the N–H bond around the C–N linkage exhibits an energy barrier. In fact, the UHF SCF geometry optimization shows that the energy maximum occurs at ω = 100°, i.e., close to a structure which may be called the face-to-face (FF) conformations[25] (see Figure 7). However, the calculated rotational barrier with respect to the FE_t conformation is as low as 1.5 kcal/mol.

Both the FE_c and FE_t conformations belong to the point group C_s symmetry. The CI treatments show that both of them can most adequately be described by a single-configuration:

$$^3FE(A''):\ (1a')^2 \ldots (6a')^2(1a'')^2(7a')^2(8a')^2(2a'')^2(3a'') \times (9a')^2(10a')$$

The weights of this main configuration in the CI expansion are

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(25) Fueno, T.; Yamaguchi, K.; Kondo, O., to be submitted for publication.

Table VII. Comparison of Various Conformations for the Singlet Diradical State of CH_2CH_2NH

	conformations			
	^{1}EF ($\omega = 90°$)	^{1}EF$_t$ ($\omega = 180°$)	^{1}FF ($\omega = 90°$)	^{1}FE$_t$ ($\omega = 180°$)
relative energies, ΔE (kcal/mol)[a]				
CI, $T \rightarrow 0$	4.9	−0.6	−4.7	3.6
"full" CI	5.5	−1.1	−4.1	2.8
weight of leading configurations				
$c_1{}^2(\lvert\overline{a}b\rangle)$	0.931	0.889	0.737	0.921
$c_2{}^2(\lvert a^2\rangle)$	<0.001	0.017	0.176	<0.001
$c_3{}^2(\lvert b^2\rangle)$	<0.001	0.008	0.021	<0.001

[a] The extrapolated ($T \rightarrow 0$) and "full" CI energies for the ^{3}FE$_t$ conformer as the reference points are −133.0274 and −133.0445 hartrees, respectively. The triplet SCF MO's are employed in the CI treatment.

0.927 and 0.926 for ^{3}FE$_c$ and ^{3}FE$_t$, respectively. The MO 3a″ is localized largely on the nitrogen atom and can be characterized by the $p_y(\pi)$ orbital perpendicular to the plane of the CCN skeleton, while the MO 10a′ is essentially the carbon $p_x(\sigma)$ orbital, which lies in the CCN plane and is orthogonal to the C–C linkage.

In addition to the above-described two FE conformations, there exists a third stable conformer.[25] It results from the ^{3}FE$_t$ conformer by placing the terminal methylene hydrogen atoms in the plane of the heavy atoms (cf. Figure 7). This "coplanar" structure, which may be referred to as the ^{3}FE$_t$ conformer (Figure 7), has also the C_s symmetry. The expansion of the CI wave function for this conformer contains the leading contribution of a single configuration:

$$^3\mathrm{EE_t(A')}:\ (1a')^2\ldots(7a')^2(1a'')^2(8a')^2(9a')^2(2a'')(10a')^2(3a'')$$

with the weight of 0.928. Here also, the singly occupied MO's, 2a″ and 3a″, are localized mainly on the nitrogen and carbon atoms, respectively. The SCF CI ($T \rightarrow 0$) and "full" CI energies calculated for this ^{3}EE$_t$ conformer with the 4-31G basis set are 5.6, 0.4, and −0.5 kcal/mol, respectively, relative to the separated $NH(^3\Sigma^-)–C_2H_4$ system. Most likely, ^{3}EE$_t$ is the most stable form for the triplet CCN diradical.

We now turn our attention to the singlet state of the CCN diradical. Possible conformations yielding local energy minima for the singlet CCN are not necessarily similar in structure to those for the triplet CCN diradical. The UHF SCF geometry optimization treatment[25] shows that the FE$_t$ conformation is indeed an energy minimum for the singlet CCN as well. However, the FE$_c$ conformation, which represents another energy minimum in the case of triplet CCN, appears as a local energy maximum with respect to the rotation angle ω for the singlet state. Instead, the FF ($\omega = 90°$) structure, which is nearly on the top of the rotational barrier for triplet CCN, has now been found to be nearly at the bottom of the potential energy curve with the rotational barrier shifted at $\omega = 130°$. This last ^{1}FF-type conformer has been found to be even more stable than ^{1}FE$_t$(A″). In addition to those two stable geometrical configurations, the diradicals ^{1}EF and ^{1}EE$_t$(A′) (see Figure 7) with the methylene hydrogen atoms lying in the CCN plane are also conceivable. All four geometries have been determined separately by the singlet UHF SCF geometry optimizations.[26] Note that neither ^{1}FF nor ^{1}EF has spatial symmetry.

In Table VII the results of the three-reference (3M) CI treatment with energy selection threshold $T = 10$ μhartrees for the four singlet CCN diradical forms are compared. The three leading configurations:

$$|a^2\rangle = (\phi_1\alpha)\ldots(\phi_{N-1}\beta)(a\alpha)(a\beta)$$

$$|b^2\rangle = (\phi_1\alpha)\ldots(\phi_{N-1}\beta)(b\alpha)(b\beta)$$

$$|\overline{a}b\rangle = (\phi_1\alpha)\ldots(\phi_{N-1}\beta)(2^{-1/2})[(a\alpha)(b\beta) - (a\beta)(b\alpha)]$$

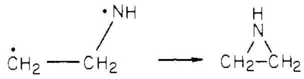
differ in the occupation numbers of the frontier MO's a(HOMO) and b(LUMO). The triplet SCF MO's are employed for building up the singlet CI spaces because the open-shell singlet SCF Roothaan procedure is not applicable to all these conformers (e.g., for the $A'(C_s)$ structures). The closed-shell singlet SCF procedure is obviously inadequate for the description of such biradical geometries. As expected, the electronic configuration $|\overline{a}b\rangle$ has a dominant role in the correlated singlet wave functions.

Inspection of the data given in Table VII reveals that among all singlet CCN conformers considered the ^{1}FF conformer is the most stable. Moreover, it lies lower in energy than any of the considered triplet states examined. The singlet CI wave function of ^{1}FF conformer exhibits besides the large weight of $|\overline{a}b\rangle$ configuration (0.737) also a contribution of the closed-shell configuration $|a^2\rangle$ with the weight of 0.176. It is worth mentioning that the occupation numbers of the two natural orbitals which represent correlated analogues to the HOMO and LUMO are found to be 1.281 and 0.612, respectively. These results indicate that the ^{1}FF conformer exhibits "biradicaloid" features and not a pronounced biradical character as do those biradicals for which there exist two natural orbitals with the occupation numbers very close to unity.[27] The described result may be brought in connection with the fact that the ^{1}FF conformation is structurally the most closely related to aziridine, which is a ring-closed form in the electronic ground state.

The second most stable form of singlet CCN is ^{1}EE$_t$. However, it is somewhat less stable than ^{3}EE$_t$; the CI extrapolated energies ($T \rightarrow 0$) of ^{1}EE$_t$ and ^{3}EE$_t$ relative to the common reference point ^{3}FE$_t$ are −0.6 and −2.5 kcal/mol, respectively. It has been found also in the case of trimethylene that the ^{3}EE$_t$ has greater stability than its singlet structure.[28]

The singlet states which contain the largest dominant contribution from the closed-shell electronic configuration $|a^2\rangle$ are generally far less stable than the corresponding biradical states. Such singlet states are of zwitterionic nature and accommodate an excess of electronic charge mainly on the nitrogen p orbitals, leaving the terminal carbon atom positively charged. The most stable form of these zwitterionic singlet states is found to be also a ^{1}FF conformer. This excited singlet state (^{1}FF^{zw}) lies 63 kcal/mol above the ^{1}FF diradical (CI, $T \rightarrow 0$ energies are compared). Notice, that the closed-shell electronic configuration $|a^2\rangle$ mixes with the open-shell configuration $|\overline{a}b\rangle$ in the ^{1}FF diradical state. In contrast, these two configurations cannot mix in the singlet state of ^{1}FE$_t$(A″) conformer because they belong to two different irreducible representations (A′ and A″) of the C_s point group. Consequently, the excited singlet state ^{1}FE$_t{}^{zw}$ of the ^{1}FE$_t$ conformer lies much higher in energy than the most stable zwitterionic state ^{1}FF^{zw}. The energy gap between ^{1}FF$_t{}^{zw}$ and ^{1}FE$_t$ is 90 kcal/mol.

B. Cyclization into Aziridine. The CCN diradical should formally yield aziridine upon ring closure:



(5)

The purpose of this subsection is to elucidate how the various diradical states of CCN can be correlated with different electronic states of aziridine. The diradical states here considered are ^{1}FF ($\omega = 90°$) and ^{1,3}FE$_t$ ($\omega = 180°$). The ^{3}FE$_c$ ($\omega = 0°$) state was not considered because of its similarity in behavior to the ^{3}FE$_t$ conformer.

The course of cyclization has been followed computationally by taking the CCN bond angle θ as the principal reaction coordinate. The internal coordinates used for the region $\theta > 90°$ are the same as in Figure 5. In the region $\theta < 90°$, a subsidiary axis

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[26] Geometry optimization has shown that, among the four singlet diradical forms considered, the ^{1}EF structure cannot be a local minimum. It corresponds to the top of the potential energy curve for the direct isomerization of ^{1}EE$_t$ into ^{1}FF.[25]

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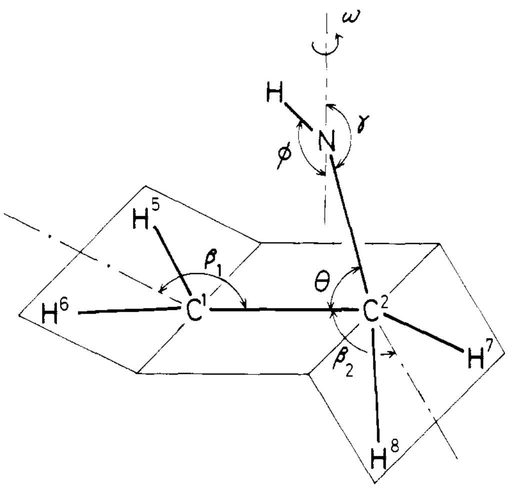

Figure 8. Internal coordinates used for the cyclization of CH_2CH_2NH to aziridine.

Table VIII. Selected Path Points for Tracing the Cyclization of CH_2CH_2NH to Aziridine

	path point					
angle	I (aziridine)	A	B	C	D	J^a (CCN)
θ (deg)	60.2	70.0	80.0	90.0	100.0	111.8
β_1 (deg)	200.6	194.0	188.0	180.0	174.5	166.5
β_2 (deg)	159.4	153.0	147.0	140.0	135.0	128.7
γ (deg)^b	150.2	160.0	170.0	180.0	180.0	180.0
ω (deg) ^{1}FF	90.0	90.0	90.0	90.0	90.0	90.0
$^{1,3}FE_t$	180.0	180.0	180.0	180.0	180.0	180.0
ϕ (deg) ^{1}FF	112.0	112.0	112.0	112.0	112.0	109.5
$^{1,3}FE_t{}^c$	180.0	112.0	112.0	112.0	112.0	109.5

[a] Based on the optimized geometry for the ^3FE_t diradical. [b] $\gamma = \theta + 90°$ when $\theta < 90°$ (Figure 7), while $\gamma = 180°$ when $\theta \geqslant 90°$ (Figure 5). [c] The N–H bond at path points *A–J* as well as at path point *I* is coplanar with the CCN plane because of $\omega = 180°$.

which passes through the nitrogen atom and is perpendicular to the C–C bond has been introduced, as shown in Figure 8. The values of θ for ground-state aziridine and the ^3FE_t diradical are 60.2 and 111.8°, respectively. For the sake of convenience, these angles are assumed to remain the same for other electronic states. Between these two limiting structures, four additional path points, which are characterized by θ = 70, 80, 90, and 100°, respectively, have been selected for computation. The angles which vary most markedly with the change in θ are β_1 and β_2. Instead of performing geometry optimization at each given θ, we have assumed here that both β_1 and β_2 vary proportionally with the change in θ. The values adopted for these two angles at different path points are given in Table VIII together with other pertinent angle variables. The remaining internal coordinates (bond distances as well as the bond angles) are all assumed to be the same as in ground-state aziridine. The assumption seems to be justifiable since none of these distances and angles differ appreciably between aziridine and the ^3FE_t diradical.

Figure 9 shows how the CI, $T \rightarrow 0$ energies calculated for the ^{1}FF, $^1FE_t(A'')$, and $^3FE_t(A'')$ diradicals change with the variation in θ. The ^{1}FF diradical, which is the most stable form of CCN, is stabilized continuously with decreasing θ, until it settles down to aziridine in the ground electronic state (S_0). It seems that in the CI, $T \rightarrow 0$ limit no barrier exists along this pathway. On the other hand, the ^1FE_t and ^3FE_t conformers become strongly destabilized, reaching eventually the first excited singlet (S_1) and triplet (T_1) states of aziridine, respectively. Although these calculations are not based on fully optimized geometries, the results appear to be sufficiently clear in order to correlate the states. Note that $^1FF_1$ cyclizes, keeping its N–H bond out of the CCN plane all the way, while both ^1FE_t and ^3FE_t which retain the N–H bond in the plane, smoothly reach the excited aziridine in the "planar" form. The ground-state (S_0) aziridine is in fact in C_s symmetry with the pyramidalized imino moiety, whereas the excited (S_1 as well as T_1) aziridine is determined to have the structure of C_{2v} symmetry.

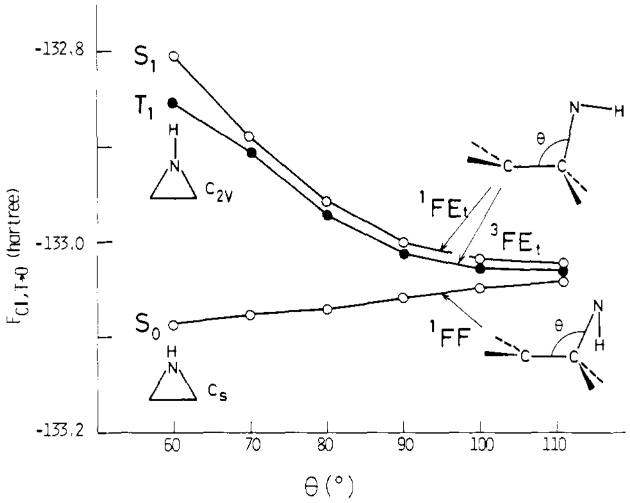

Figure 9. The extrapolated CI ($T \rightarrow 0$) energies as the functions of the bond angle θ for the ^1FE_t, ^3FE_t, and ^{1}FF diradicals. The 3M/1R (T = 10 μhartree) treatment with triplet SCF MO's is employed for all the points except for aziridine. For the ground state (S_0) of aziridine in C_s symmetry, a 2M/1R CI (T = 10 μhartree) procedure with closed-shell singlet SCF MO's is employed. For the triplet (T_1) and first excited singlet (S_1) states in the C_{2v} symmetry, the 1M/1R (T = 10 μhartree) CI procedure with triplet SCF MO's is used.

Examination of the CI expansion coefficients indicates that in the case of the ^1FE_t–S_1 and the ^3FE_t–T_1 correlations, the "biradical" open-shell configuration $|a\bar{b}\rangle$ is invariantly the most dominant of all. The contribution of this main configuration, in which one of the unshared electrons is accommodated in the nitrogen p_π atomic orbital, has exceeded 0.89 at any of the path points studied.

The situation for the ^1FF–S_0 state contrasts significantly. For this case the results of the three-reference CI treatment (3M/1R) at the various path points are given in Table IX. From path point J to I, the weight of the $|a\bar{b}\rangle$ configuration diminishes strongly, allowing the $|a^2\rangle$ configuration to take over the share progressively. Also, the values of occupation numbers n and n' of two characteristic natural orbitals change gradually, demonstrating a transition from the "biradicaloid" structure at the point J toward the closed-shell species at the point I. For path points A–J, the triplet SCF MO's were used to build up the CI spaces for the singlet states. Note how smoothly both the CI, $T \rightarrow 0$ energy and CI coefficients of the leading configurations approach those for the ground-state aziridine for which the one-reference CI treatment with the closed-shell singlet MO's has been employed.

VII. Discussion

The relative energies of the low-lying electronic state ($^3\Pi$, $^1\Sigma^+$, $^1\Delta$, and $^3\Sigma^-$) of the NH radical calculated by the MRD-CI procedure with the conventional 4-31G basis set are found to be in fair agreement with observation. The relative energies of the minima for $^1\Delta$, $^3\Pi$, and $^3\Sigma^-$ states determined by the open-shell and triplet SCF procedure, respectively, do not change substantially in the CI treatments. However, the $^1\Delta$–$^3\Sigma^-$ energy gap obtained from the SCF or CI treatments with the 4-31G basis set is not yet in good agreement with the experimental value (Table I). Inclusion of polarization functions in the basis (B and D from Table I) tends to improve the CI results of the energy gap, but the smallest energy gap which we obtained is still ca. 5 kcal/mol larger than the experimental value. Further investigation of the influence of very large basis sets and higher excitations than doubles with respect to the reference configurations in the CI treatment on the singlet–triplet energy gap is not attempted here. A large-scale CI treatment applied by Saxe et al.[29] for deter-

Table IX. The CCN(^{1}FF)-Aziridine (S_0) Correlation Obtained by the CI Treatment Employing Triplet SCF MO's

	path point					
	I	A	B	C	D	J
θ (deg)	60.2	70.0	80.0	90.0	100.0	111.8
rel energies (kcal/mol)[a]						
CI, $T \rightarrow 0$	−30.3[b]	−27.2	−23.0	−12.6	−7.1	0[c]
"full" CI	−35.3[b]	−33.1	−26.9	−19.7	−9.2	0[c]
configurations						
$c_1{}^2(\|a^2\rangle)$	0.908	0.868	0.844	0.676	0.484	0.176
$c_2{}^2(\|\overline{a}b\rangle)$	0.000	0.026	0.048	0.201	0.409	0.737
$c_3{}^2(\|b^2\rangle)$	0.000	0.009	0.022	0.019	0.029	0.021
occupation numbers of two natural orbitals[d]						
n	1.97	1.94	1.91	1.84	1.69	1.38
n'	0.02	0.05	0.09	0.16	0.30	0.61

[a] The CI energies were obtained by three-reference, one-root (3M/1) CI treatment with the selection threshold $T = 10$ μhartrees. [b] Results obtained by the two-reference CI ($|a^2\rangle$ and $|b^2\rangle$) treatment with $T = 10$ μhartrees employing closed-shell singlet SCF MO's. The CI, $T \rightarrow 0$, and "full" CI energies are −133.0831 and −133.1073 hartrees, respectively. [c] The CI, $T \rightarrow 0$ and "full" CI energies for the ^{1}FF CCN diradical as the reference point are −133.0348 and −133.0510 hartrees, respectively. [d] Two natural orbitals are correlated analogues to the HOMO and LUMO.

mination of the energy gap $^1A_1 - {}^3B_2$ for CH_2 might settle this problem. However, this is out of the primary scope of the present work which aims to investigate the reaction of NH with hydrogen and ethylene.

The insertion reaction of NH($^1\Delta$) to H to give NH_3 ($\tilde{X}^1A_1$) is without doubt a thermally favorable process; there is no activation barrier at all. Insertion of NH($^3\Pi$) leading to the formation of $NH_3(\tilde{a}^3A_2'')$ is also predicted to be a fairly easy process. The barrier of ca. 7.6 kcal/mol (at $R = 1.3$ Å) which results from SCF calculations is virtually washed out by inclusion of correlation effects. Nishi et al.[30] have recently determined the collisional decay rates of NH($^3\Pi$) generated by the laser photolysis of methylamine. The rate constants observed for the decay of NH($^3\Pi$) in collision with various neutral species show that NH($^3\Pi$) undergoes quenching for almost every collision. They note that the decay is not due to a physical quenching of NH($^3\Pi$) to lower electronic states but is likely to be a chemical process. Our CI potential energy curve strongly suggests the possibility that the observed decay process is the insertion reaction. The insertion is characterized as a least motion process which proceeds with the $B_1(C_{2v})$ structure maintained throughout its course.

The state correlations between the NH+ H_2 system and the molecular NH_3 have already been studied by Runau et al.[31] in connection with the photo-dissociation of NH_3. However, their correlation curves can hardly be compared with ours because of the very different geometrical constraints they used. For example, they have calculated other components of the NH($^1\Delta$) + H_2 state which correlates with highly excited state as H_2 approaches NH. Further, the potential curve for NH($^3\Sigma^-$) + H_2 was not considered at all. Our interest has been directed toward the thermal processes of the NH-H_2 interaction. For this purpose geometry optimizations have been carried out. The only case common to these two studies is that of the NH($^3\Pi$)-H_2 system.

The minimum-energy path for the interaction of NH($^3\Sigma^-$) with H_2 is actually the one leading to the formation of NH_2 + H. The activation barrier height calculated for this abstraction reaction is 24 kcal/mol. The abstraction reaction is therefore far less efficient than an analogous reaction of O(^{3}P), for which the experimental activation energy has been evaluated to be 9.9 kcal/mol at 500 K.[32]

The addition of NH($^3\Sigma^-$) to ethylene is likely to be a more favorable process than its hydrogen abstraction from H_2. The smallest activation barrier height we obtained was 11.8 kcal/mol. The NH($^3\Sigma^-$) addition seems to take place less easily than does a similar reaction of $CH_2(^3B_1)$ for which a calculated barrier height of 5.0 kcal/mol has been reported.[33] Likewise, it is less favorable than the addition of O(^{3}P), for which the experimental activation energy is 1.6 kcal/mol.[34] The relatively large barrier heights obtained for the NH($^3\Sigma^-$) reactions can be taken as an indication of the innately larger stability of NH($^3\Sigma^-$) as compared with its isoelectronic homologues $CH_2(^3B_1)$ and O(^{3}P). This in turn partly accounts for less knowledge about chemical reactions with NH($^3\Sigma^-$).

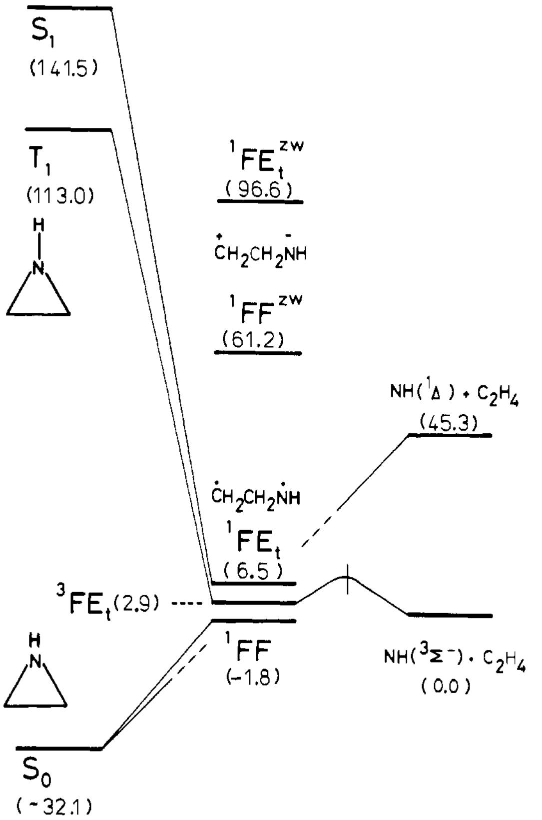

Figure 10. Schematic energy level diagram for the chemical processes involving NH and C_2H_4. The energies (in kcal/mol) appended to the state levels are relative to the isolated NH($^3\Sigma^-$) + C_2H_4 system.

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Finally, a brief summary of the energetics for various chemical processes involving the CCN diradicals is given in Figure 10 in which a schematic diagram contains different states for the NH + C_2H_4 system, CCN diradicals, and aziridine obtained from the dscribed CI, $T \rightarrow 0$ treatments. The relative energy levels for the same system have already been considered by Haines and Csizmadia.[6] It should be noted here that their singlet CH_2CH_2NH correlated with the aziridine S_1 state seems to correspond to our zwitterionic state $^1FE_t^{zw}$ with a dominant contribution of $|a^2\rangle$ configuration. It is easy to depict from Figure 10 that the ^1FF diradical state correlates without doubt with the ground-state S_0 of aziridine.

One important facet which has totally been left out of consideration in this work is the problem concerning courses of isomerization for the CCN diradical other than the cyclization. This point, together with the overall kinetic phase of the $NH(^3\Sigma^-)$-ethylene reaction, will be reported elsewhere.

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Registry No. NH, 13774-92-0; H_2, 1333-74-0; $CH_2{=}CH_2$, 74-85-1; $\cdot CH_2CH_2NH\cdot$, 86239-28-3.

Theoretical Investigation of the Elimination and Addition Reactions of Methane and Ethane with Nickel

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Abstract: Contracted CI calculations have been performed to study the mechanisms for the concerted elimination and addition reactions of ethane and methane with nickel. It is found that the $^1A_1$ state of nickel–ethane and the $^1A'$ state of nickel–methane behave very similarly. The elimination barrier, for example, is computed to be 34 kcal/mol for methane and 37 kcal/mol for ethane. For the addition reaction a somewhat larger difference is obtained, the activation energy of methane being 54 kcal/mol and of ethane (breaking the C–C bond) 42 kcal/mol. This difference in activation energy can be explained by the difference in the bond strength of the C–H bond in methane and the C–C bond in ethane, the C–H bond being 16 kcal/mol stronger. The difference between these two systems on one side and H_2 on the other is large; H_2 has a computed addition barrier to nickel of only 3 kcal/mol. The hydrogen atoms can much more easily form bonds in several directions at the same time than methyl groups, and this difference leads to higher activation energies for reactions involving methyl groups. For all three systems the reaction takes place with nickel in a d^9 state and with a large extent of d involvement in the bonding at the bent equilibrium geometry.

1. Introduction

In many catalytic processes involving transition metals the formation of new bonds occurs via reductive elimination reactions, and bonds are broken via oxidative addition reactions. The mechanisms for these two types of reactions, which are the reverse of each other, can be either concerted or nonconcerted. The nonconcerted reaction should in this case have a radical mechanism which would involve high activation energies. The purpose of the present study is therefore to investigate the concerted reaction mechanisms for different types of reactants. A homogeneous reductive elimination and oxidative addition reaction can be written:

$$L_nMR_1R_2 \rightleftarrows L_nM + R_1{-}R_2 \qquad (1)$$

where M is a transition metal, the L's are nonreacting ligands (type phosphines or carbonyls), and the reacting group R_1 and R_2 are hydrogen atoms or alkyl groups. From experiment it is well known that the ligands L can have a great influence on the reaction rate. The activation energy for elimination of butane from diethyl(dipyridyl)nickel is, for example, reduced from 66 to 16 kcal/mol upon complexation of an olefin.[1] The approach we have chosen is, however, to build up an understanding of these kinds of reactions from as simple models as possible, where we can study the electronic mechanisms of the bond-breaking and bond-forming processes in detail and then step by step investigate how different factors can influence the reaction. We have, therefore, not included any ligands L in this study in order to obtain accurate results for the pure elimination and addition reactions. The effects of different types of ligands are under investigation and will be presented in later papers.[2] Our specific purpose in this paper is to compare reaction mechanisms for the three classes of reactions represented by different combinations of R groups, H–H, H–alkyl, and alkyl–alkyl, and try to correlate these to experimental reaction rates. Methyl groups are used as models for alkyl groups and nickel for the transition metal. The results for H–H have been presented in previous papers on NiH_2[3] and will only be repeated here for the sake of comparison. In the present paper the details of the results for $Ni(H)CH_3$ and $Ni(CH_3)_2$ will be presented. In a forthcoming paper comparisons between nickel and palladium compounds will be presented together with the effects of introducing water ligands into the model.[4] Some of the results have been discussed earlier in ref 5.

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