

Nonempirical Calculations of the Reaction Surface for the Addition of the Amino Radical to Ethylene

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Abstract: *Ab initio* SCF and CI calculations of the reaction surface for the addition of the amino radical $\text{NH}_2\cdot$ to ethylene are reported. It is found that greater flexibility in the AO basis employed in the theoretical treatment is required to obtain a balanced treatment for both reactants and products than is generally necessary for the accurate description of a single equilibrium structure. The calculations indicate that reactions of this type are best described in terms of two distinct potential curves: one attractive, representing the formation of a CN bond; the other repulsive, characterizing the interaction between nitrogen nonbonding electrons and the olefinic center. The transition state for this reaction occurs for $R_{\text{CN}} \cong 3.8$ bohrs, with the change of hybridization at the central carbon from sp^2 to sp^3 approximately 60% complete at this point; the calculated activation energy is in the 35–40-kcal/mol range, a result which is consistent with the known inactivity of neutral amino radicals in addition reactions. The CI method is shown to be necessary to obtain a smooth transition between the aforementioned repulsive and attractive potential curves but is seen to play only a relatively minor role in adjusting the relative stability of the reactants and products.

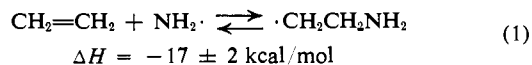
Although the existence of neutral amino radicals has been known for some time, characterization of both their nature and their reactivity has received very little attention until very recently. As in the case of most radicals there are only a few general reactions which amino radicals might be expected to undergo, the most obvious of which are combination and disproportionation, displacement of a hydrogen atom (abstraction), and addition to an unsaturated center.

The abstraction reaction for amino radicals has been examined by several authors. Mackay and Waters² have reported that the dimethylamino radical is not an efficient dehydrogenating agent. It has been found in this laboratory that the same radical abstracts hydrogen from both toluene and cumene at 136°, albeit reluctantly,^{3a} but that the analogous reaction with tri-*n*-butyltin hydride proceeds in essentially quantitative yield.^{3b} The relative rates of abstraction from substituted toluenes give an excellent correlation with σ^+ values,⁴ yielding a negative ρ value (−1.1) and thereby indicating that the transition state for this reaction is destabilized by electron-withdrawing substituents. The rate study in question is also in qualitative agreement with that reported earlier by Johnston, *et al.*⁵

The situation with regard to the addition reactions of these species is much less clear. To date no addition of simple neutral amino radicals to simple doubly bonded systems has been observed in solution; attempted additions of the dimethylamino radical to cyclohexene, norbornene, *trans*-dichloroethylene,⁶ 1-nonenone,⁷ and *tert*-butylethylene, respectively, have been

uniformly unsuccessful. The gas-phase addition of this species to ethylene has been reported⁸ at elevated temperatures (127–175°), however, but the attempted addition of the simplest amino radical $\text{NH}_2\cdot$ to cyclohexene has failed.⁹

The apparent inactivity of amino radicals with respect to addition reactions would seem to indicate a high value for the activation energy in such processes. According to thermochemical calculations the prototype reaction involving addition of $\text{NH}_2\cdot$ to ethylene is actually exothermic by a fairly wide margin.¹⁰



The question of why the transition state in this reaction is so relatively unstable with respect to both reactants and products would therefore seem to be crucial in the understanding of the behavior of the amino radical in addition to olefinic systems. It is the purpose of this paper to investigate these energy relationships for reaction 1 by means of theoretical *a priori* calculations.

General Considerations Concerning the Theoretical Method

It is well known that the Hartree-Fock method is generally incapable of obtaining a reliable description of the potential surface associated with the decomposition of a bound system.¹¹ The single configuration electronic wave function employed in this method is in the majority of cases better suited for the representation of each of the products of decomposition than the system in its combined form; as a result the calculated

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(1) Currently on leave of absence at the Eidgenössische Technische Hochschule (Zürich).

(2) D. Mackay and W. A. Waters, *J. Chem. Soc. C*, 813 (1966).

(3) (a) C. J. Michejda and W. P. Hoss, *J. Amer. Chem. Soc.*, **92**, 6298 (1970); (b) D. Cambell and C. J. Michejda, unpublished data.

(4) J. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(5) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc. B*, 1114 (1966).

(6) W. P. Hoss, Ph.D. Thesis, University of Nebraska, 1971.

(7) B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961).

(8) A. Good and J. C. J. Thyne, *J. Chem. Soc. B*, 684 (1967).

(9) Y. Ogata, Y. Izawa, and H. Tomioka, *Tetrahedron*, **23**, 1509 (1967).

(10) The heat of reaction calculated from the appropriate bond dissociation energies (S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965)) is −19 kcal/mol, while that found by utilizing the heats of formation of ethylamine, ammonia, H_2 , and ethylene is somewhat higher, −15 kcal/mol.

(11) For example, G. Das and A. C. Wahl, *J. Chem. Phys.*, **44**, 87 (1966).

dissociation energy is generally underestimated in this method. This deficiency is directly related to the existence of the so-called correlation energy error inherent in the Hartree-Fock method.

If the number of closed shells remains the same throughout the decomposition process the variation of the correlation energy becomes a much less critical factor. The decompositions of NeH^+ and HeH^+ respectively (into H^+ and rare gas atom) are examples which demonstrate the validity of this general principle.¹² Application of this result to the present situation, in which both the combined system and the sum total of its reactive fragments contain only a single open shell with the same number of closed shells, would seem to lead to the conclusion that the difference in correlation energy error should be of minor importance in this case, so that the Hartree-Fock method by itself should be able to give an adequate description of the reaction surface for the addition of amino radicals to olefins.

Despite this general conclusion there are in practice at least three additional factors which may affect the outcome of such energy surface calculations. First, the above theoretical argument is valid only in a qualitative sense and does not preclude errors in the calculated separation energy of the magnitude of several kilocalories per mole. Fortunately errors of this type can be compensated for by the method of configuration interaction (CI), which can be carried out without any substantial increase in the degree of difficulty in the overall theoretical method.

The second factor is perhaps more significant and stems from deficiencies in the AO basis set chosen for the theoretical study; for practical reasons it will necessarily be of less than Hartree-Fock accuracy in the treatment of the present problem. Experience has shown that SCF calculations employing a quite restrictively grouped basis set¹³ (but one which is capable of obtaining a good approximation to the Hartree-Fock orbitals of the constituent atoms) are quite successful in describing the potential surfaces of polyatomic systems near equilibrium,¹⁴⁻¹⁷ but they cannot be expected to give an equally good description for the entire energy surface because such functions are quite naturally less accurate for molecules than for the respective separated atoms for which they are particularly optimized. It is thus apparent that a possible effect due to an increase in the flexibility of the basis set toward molecular Hartree-Fock accuracy should not be overlooked.

Finally it should be recognized that even if an exact theoretical treatment were available for the study of this prototype reaction, a complete optimization of all geometrical parameters of the system in question at each point along the reaction path is not practical. Since more is known experimentally concerning the stereochemistry of the bound species in this or any other reaction, there will clearly be a tendency in such calculations to overestimate the barrier to formation of the transition state as a result of the incomplete optimization of the various geometrical parameters at each stage of the reaction.

(12) S. Peyerimhoff, *J. Chem. Phys.*, **43**, 998 (1965).

(13) J. L. Whitten, *ibid.*, **44**, 359 (1966).

(14) R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *ibid.*, **46**, 2029 (1966).

(15) S. D. Peyerimhoff, *ibid.*, **47**, 349 (1967).

(16) S. D. Peyerimhoff and R. J. Buenker, *ibid.*, **51**, 2528 (1969).

(17) S. D. Peyerimhoff and R. J. Buenker, *ibid.*, **49**, 2473 (1968).

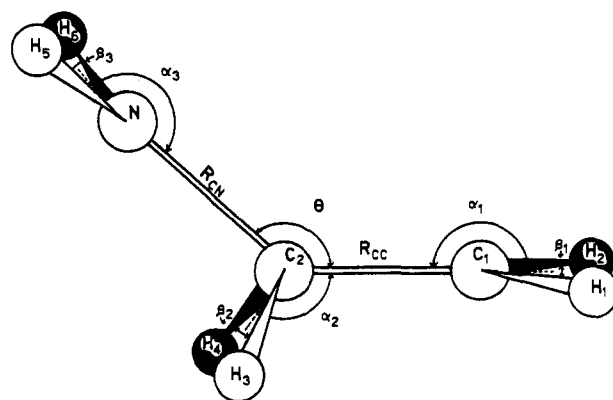


Figure 1. Definition of geometrical parameters for the C_2NH_5 system.

Fixed Group SCF Treatment of the Reaction Surface

A. Geometry of Reactants and Product. The basis set used for determining the theoretical equilibrium geometries of the combined radical $\cdot\text{CH}_2\text{CH}_2\text{NH}_2$ and the reactant species ethylene and $\text{NH}_2\cdot$ consists of a series of fixed group Gaussian lobe functions of near Hartree-Fock accuracy for the atoms; details of this basis set may be found elsewhere.^{13,14} It employs 105 primitive Gaussian functions grouped into 24 fixed linear combinations which serve as the actual basis functions for the SCF treatment.

The product of the reaction has been assumed to be the β -aminoethyl radical; the alternative isomeric ringed system has not been considered in this study. Definition of the various geometrical parameters which need to be considered is given in Figure 1, while the values for these quantities ultimately taken to correspond to the equilibrium structure of the β -aminoethyl radical are contained in Table I.

The optimum value of θ found in this treatment (115°) is in good agreement with that predicted from consideration of Walsh's rules^{18,19} for a 25-electron (19 valence electrons) species with a triatomic skeleton. The calculated CC and CN distances are approximately 0.05 \AA greater than their respective experimental values; overestimations of this magnitude for bond distances between heavy atoms are characteristic of fixed group SCF calculations.¹⁴

In all calculations to be considered the orientation of the central methylene group is chosen to be perpendicular to the CCN plane (assuming sp^3 hybridization at the central carbon). For the NH_2 species and the terminal CH_2 group four different geometrical arrangements (coplanar and perpendicular to the CCN plane) have been investigated by means of SCF calculations. The most stable orientation is found to be that in which the terminal CH_2 is coplanar with the CCN skeleton while the amino group is perpendicular; the next most stable conformer, with both species perpendicular, is only about 0.25 kcal/mol higher in energy, while the least likely of the four arrangements is calculated to be less stable than the optimum arrangement by 1.2 kcal/mol . Since ethylene with its coplanar CH_2 groups is the separation product, however, the conformer with the terminal methylene and the amino group both perpendicular

(18) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

(19) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta*, **24**, 132 (1972).

Table I. Final Geometrical Parameters Chosen for the Reaction of $C_2H_4 + NH_2\cdot$ (Fixed Group Treatment)

Parameter ^a	Combined system		Reactants $C_2H_4 + NH_2\cdot$	
	Value	Reason for choice	Value	Reason for choice
R_{CN}	1.51 Å	Optimized independent variable	∞	
R_{CC}	1.60 Å	Three point optimization (exptl ≈ 1.54 Å)	1.40 Å	Fixed group optimum for C_2H_4 (exptl 1.34 Å)
θ	115°	Five-point optimization	Immaterial	
α_2	122.5°	Optimization at three different values of θ indicates $\alpha_2 = (360 - \theta)/2$ (i.e., bisector of θ)	180°	Assumed (exptl)
α_1	180°	Actual calculation suggests α_1 slightly greater but energy gain not important		
α_3	180°	Possibly slightly smaller, but energy increased at 140°	Immaterial	
β_1	120°	sp^2 hybridization assumed	120°	Assumed (exptl $\approx 117^\circ$)
β_2	108°	sp^3 hybridization assumed		
β_3	105°	Assumed	105°	Assumed
CH	1.08 Å	Assumed for all cases	1.08 Å	Assumed
NH	1.00 Å	Assumed	1.00 Å	Assumed
$C_1H_1H_2$ plane	\perp^b	Actual calculation indicates that coplanar arrangement is slightly better ($\Delta E = 0.0004$ hartree)	\perp^b	Assumed
$C_2H_3H_4$ plane	\perp^b	Assumed (sp^3 hybridization)		
NH_5H_6 plane	\perp^b	Optimized, but not critical	Immaterial	

^a See Figure 1 for definition. ^b Perpendicular with respect to the NCC skeleton.

Table II. Variation of R_{CC} , α_2 , and β_2 (see Figure 1) with the Hybridization Factor γ^a

	γ 0.0	0.2	0.4	0.5	0.6	0.8	1.0
R_{CC} , Å	1.40	1.44	1.48	1.50	1.52	1.56	1.60
α_2 , deg	180	168.5	157.0	151.25	145.5	134.0	122.5
β_2 , deg	120	117.6	115.2	114.0	112.8	110.4	108

^a In this definition $\gamma = 0.0$ corresponds to separated reactants, $\gamma = 1.0$ to the combined system at equilibrium.²³

lar to the CCN plane has been chosen to represent the structure of the combined radical for the purpose of obtaining a suitable reaction path for this process.

The structures of the reactant species are based almost exclusively upon experimental findings²⁰ (see Table I). The lone exception is the value chosen for R_{CC} in ethylene; by analogy with the results of other fixed group SCF determinations of bond distances between heavy atoms,¹⁴ it was decided to employ a value approximately 0.05 Å greater than the corresponding experimental quantity (exptl $R_{CC} = 1.34 \pm 0.01$ Å).²⁰

B. Definition of Reaction Parameters. Once the geometries of reactants and the product have been obtained the determination of the minimum energy path (presumably the reaction path) connecting these systems involves the straightforward calculation of the total energy as a function of one independent variable under the condition of systematic optimization of each of the other structural parameters at each point along the path. As in previous work with the isomerization of cyclobutene and butadiene^{21,22} it will be necessary to restrict the number of variables subject to explicit optimization. The distance R_{CN} is chosen as the independent variable since it obviously must undergo the greatest change during the course of the addition (see Table I). The CC bond distance and the central CH_2 flapping angle α_2 (see Figure 1) are also subject to a major change from reactants to product and conse-

quently require optimization at each value of R_{CN} . On the other hand, the rather large force constant associated with $\angle CCN$ bending indicates that variation in this angle from its equilibrium value in the product (115°) can safely be ignored. All other structural parameters apparently remain fairly constant as the reaction proceeds, with the rather minor exception of the central HCH angle β_2 .

The geometrical changes noted above can be described concisely as resulting from a change in hybridization at the central carbon atom as the amino group approaches the ethylene molecule. It is therefore reasonable to assume that the changes which occur for R_{CC} , α_2 , and β_2 , respectively, do so more or less in concert. Under these circumstances it was decided to define an auxiliary variable γ ²³ which varies from 0 to 1 as the reaction proceeds from the separated reactants to the combined radical at equilibrium; each of the three variables R_{CC} , α_2 , and β_2 is then assumed to vary linearly with this parameter (Table II).

C. Electronic States Involved in the Reaction. In the calculation of the C_2NH_6 energy surface there is a slight complicating factor introduced by the existence of two distinct electronic states of importance. One of these corresponds to the combination of the ground states of ethylene and $NH_2\cdot$ at infinite separation; in this case the odd electron is localized at the N atom and hence this state is hereafter referred to as the N state. The other species corresponds to the ground state of the combined radical (with the odd electron at the terminal

(20) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11 (1958); No. 18 (1965).

(21) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **93**, 2117 (1971).

(22) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *ibid.*, **94**, 5639 (1972).

(23) The definition of γ is necessarily based on theoretical rather than experimental equilibrium values for the quantities involved (see Table I).

carbon) and is hereafter denoted as the C state. Of the 25 electrons in the C_2NH_6 system 20 are contained in MO's common to both states, namely those in the three inner shells, in the four CH, the two NH, and the CC $p\sigma$ orbitals, respectively (see Table III). In the

Table III. Description of the Important Electronic Configurations of the C_2NH_6 System^a

Separated molecules	VB description	Fragment MO's	MO's of combined system	
			<i>a</i>	<i>b</i>
N state				
C_2H_4	$2 \times 1s$	a_g, b_{1u}	2	
	$4 \times CH$ bonds	$a_g, b_{1u}, b_{2u}, b_{3g}$	2	2
	CC $p\sigma$ bond	a_g	1	
NH_2	$1s$	a_1	1	
	$2 \times NH$ bonds	a_1, b_2	1	1
C_2H_4	π bond	b_{3u}	1	
NH_2	p_r	a_1	1	
	p_t	b_1	1/2	
Electronic configuration $9.5 \times a, 3 \times b$				
C State				
Com- bined mole- cule	$3 \times 1s$		3	
	$4 \times CH$ bonds		2	2
	CC $p\sigma$ bond		1	
	$2 \times NH$ bonds		1	1
	CN $p\sigma$ bond (with p_r)		1	
	p_t		1	
	$p\pi$ on terminal carbon		1/2	
Electronic configuration $9.5 \times a, 3 \times b$				

^a In spite of the fact that the N and C states are equivalent from the point of view of symmetry, it is found that both species retain their identity in the SCF treatment throughout the entire course of reaction (see Figure 3).

N state the remaining five electrons are distributed among the ethylene $p\pi$ MO and the nitrogen p-type AO's (see Figure 2a). In the C state the nitrogen p AO tangential to the CN bond (Figure 2b) is doubly occupied along with the MO representing the CN σ bond, whereas the odd electron in this case is contained in a p-type AO localized at the terminal carbon.

All the orbitals sketched in Figure 2a,b are indistinguishable on the basis of symmetry (all being symmetric under reflection in the CCN plane, the only non-trivial symmetry element of the system), so that the N and C states (both $^2A'$ species) are completely equivalent from symmetry considerations. Thus one might expect that one state is transformed into the other in a continuous manner as the addition reaction proceeds (*i.e.*, R_{CN} decreases). In spite of this possibility, however, the actual SCF calculations show that both (single configuration) states retain their identity even at intermediate values of R_{CN} ; by judicious choice of starting vector it has been possible to obtain SCF solutions for both states for a large number of nuclear conformations. The total energies resulting from these various calculations are plotted in Figure 3 and show that the N state becomes progressively less stable as R_{CN} decreases while the C state exhibits the opposite behavior. At $R_{CN} \cong 3.8$ bohrs (approximately 2.0 Å) the two states become very nearly isoenergetic, but it is apparent from the figure that their corresponding potential curves do not merge in this region but rather cross with one an-

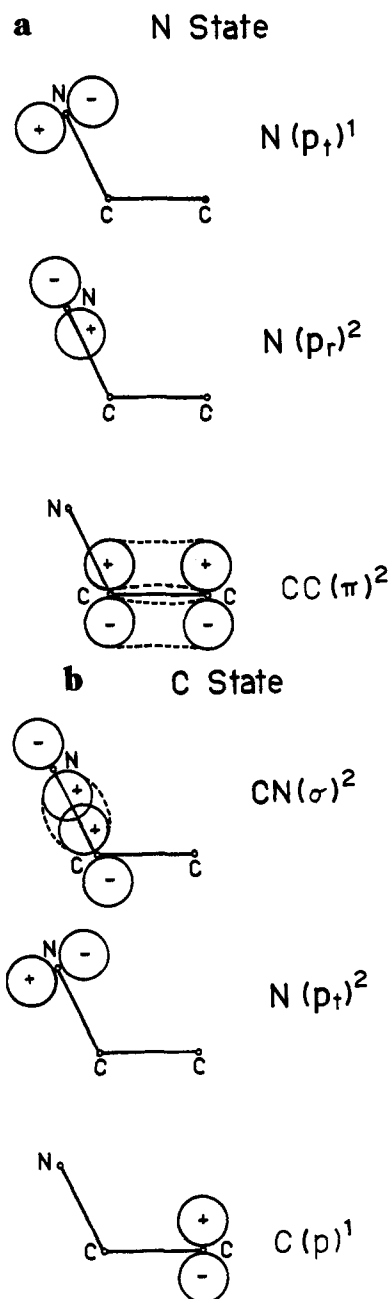


Figure 2. Schematic representation of the three highest MO's in the N state (Figure a) and the C state (Figure b); the occupation of each orbital is also indicated.

other. As a result the SCF treatment is seen to be somewhat unsatisfactory since the lack of a smooth transition between the C and N (both $^2A'$) states must clearly be an artifact of the single configuration wave function employed, for which the noncrossing rule is not valid.

CI Treatment Employing Fixed Group Basis

The aforementioned shortcoming of the SCF procedure can be removed through the introduction of configuration mixing (CI). In a full CI, in which every possible electronic configuration consistent with the Pauli principle is given explicit consideration in the expansion of the wave function, the choice of MO basis used in the construction of the various configurations is immaterial. Such a calculation for the C_2NH_6 sys-

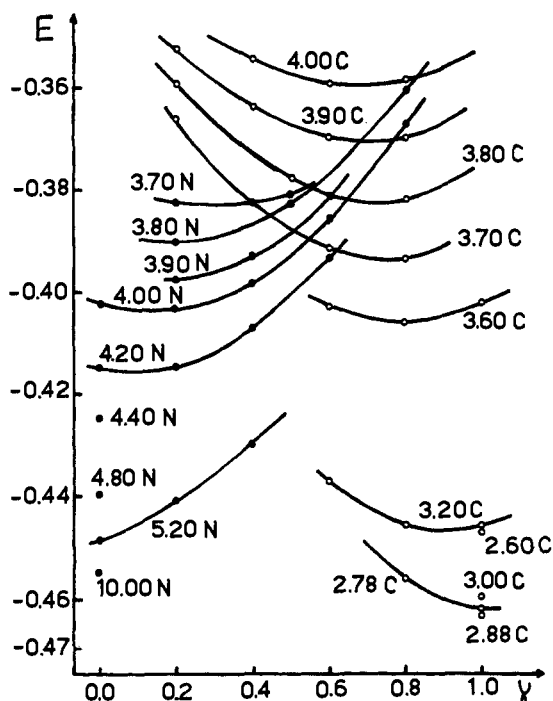


Figure 3. Total energy E (in hartrees, zero = -133.0) of the C_2NH_6 system as a function of the hybridization factor γ for N and C states at various values of R_{CN} (in bohrs, indicated at each curve), obtained from the fixed group SCF treatment.

tem under consideration is impractical at the present time, with 25 electrons to be distributed among 24 distinct MO's. It thus becomes necessary to divide the MO basis into three subsets:²⁴ a set of core orbitals which are always doubly occupied, a second (valence) set whose members are allowed variable occupation, and a third class containing the remaining species which are never allowed occupation in the CI treatment.

By restricting the possibilities for occupation of the various molecular orbitals in this way it is clear that the results do become dependent on the specific choice of the MO basis; in particular one can anticipate different results depending on whether the SCF MO's of the N state or those of the C state are used in the CI calculation. Discrepancies of this type can be kept to a minimum, however, if the linear spaces spanned by the core and valence sets (as defined above) in both cases are as nearly equivalent as possible. In the present situation this goal can be realized if all species which are chiefly composed of in-plane p AO's on carbon and nitrogen, respectively, are assigned to the valence set (six in all, three of which are shown for each case in Figure 2a,b), while all other occupied orbitals are chosen to represent the core. In what follows this type of limited CI treatment is referred to as CI(6); it requires consideration of 210 distinct configurations.

The question of the near equivalence of the two MO basis sets has been tested by means of actual calculations at the CI(6) level for C_2NH_6 structures with $R_{CN} = 3.8$ bohrs and values for γ of 0.2, 0.5, and 0.8, respectively. The values for the corresponding ground state energies resulting from the use of N state MO's, on the one hand, and those of the C state, on the other, differ by no more than 2 kcal/mol, and in two instances

(24) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta*, 12, 183 (1968).

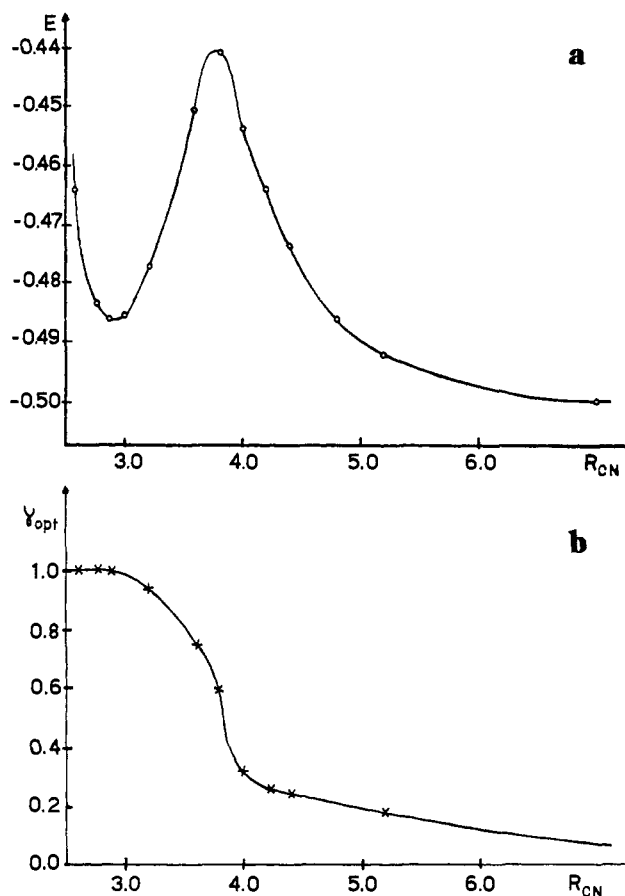


Figure 4. (a) Total energy E (in hartrees, zero = -133.0) as a function of R_{CN} (in bohrs) for the optimum γ value obtained from the CI treatment employing the fixed group AO basis. (b) The optimum γ value along the reaction path as a function of the R_{CN} distance (in bohrs).

the difference is less than 0.5 kcal/mol. These discrepancies in the CI calculations are smaller by at least a factor of 10 than those obtained by the SCF method for the corresponding nuclear geometries.

Just as in Figure 3 the reaction surface is calculated for each of the R_{CN} and γ values using the CI(6) treatment. The total C_2NH_6 ground state energy thus obtained is plotted as a function of R_{CN} under the condition of optimum γ in Figure 4a, while the variation of the optimum γ value with R_{CN} is shown in Figure 4b. A smooth transition between reactants and product is obtained as expected, although the rather strong curvature at the potential maximum is still symptomatic of the significant charge transfer which occurs as the system is converted from the N to the C state.

Details concerning the relative energetics of the transition state and the two equilibrium structures from the CI(6) treatment are compared in Table IV with corresponding data from the SCF calculations and also from experiment. The barrier is lowered significantly (by almost 10 kcal/mol) as a result of the CI, and the value of γ associated with the transition state structure is seen to represent a much greater change from that of the reactants than is found in the SCF treatment; the corresponding R_{CN} value is practically the same in both methods of calculation.

Although the CI process obtains a better description of the energy surface in the region of the transition state.

Table IV. Relative Energies and Values of R_{CN} and γ for Key Structures in the Reaction Process, Obtained Using the Fixed Group AO Basis^a

	SCF			CI(6)			Exptl		
	E	R_{CN}	γ	E	R_{CN}	γ	E	R_{CN}	γ
$C_2H_4 + NH_2 \cdot$	0.0	∞	0.0	0.0	∞	0.0	0.0	∞	0.0
Transition state ^b	46.1	3.74	0.45	37.7	3.75	0.63	?	?	?
$\cdot C_2H_4NH_2$	-5.1	2.86	1.0	8.3	2.91	1.0	-17 ± 2	2.78 ^c	1.0

^a Zero of energy for the SCF treatment is -133.4549 hartrees. Energy values are in kcal/mol, distances in bohrs. ^b Locus of crossing points of C- and N-state curves (Figure 3). ^c Represents CN distance in typical amines (1.47 Å).

it yields a value for the heat of reaction which is opposite in sign to that observed experimentally. This result is not an artifact of the particular type of limited CI considered since calculations with augmented valence sets (three additional symmetric MO's in the CI(9) treatment and all six of the antisymmetric type in the CI(12) calculation) lead to very little change in the relative energies of the various structures of interest (Table V), despite having a significant effect upon the absolute

Table V. Comparison of Energy Values Obtained from Several Calculations Employing the Fixed Group AO Basis^a

	CI(6) ^b	CI(9) ^b	CI(12) ^b
Zero of energy	-133.5000	-133.5086	-133.5290
$C_2H_4 + NH_2 \cdot$	0.0	0.0	0.0
Transition state	37.7	39.1	39.0
$\cdot C_2H_4NH_2$	8.3	10.2	8.3

^a All energy values are in kcal/mol, except for the zero-energy values, which are in hartrees (1 hartree equals 627.7 kcal/mol). ^b CI(6) includes 6a MO's in the valence set, $m = 7$. CI(9) includes 9a MO's in the valence set, $m = 7$. CI(12) includes 6a and 6b MO's in the valence set, $m = 13$. m is the number of electrons to be distributed among the orbitals in the valence set.

energies of these species. The fault must rather be sought in the restrictive type of AO basis set employed.

In the fixed group basis the contraction coefficients of the various Gaussian functions are chosen so as to minimize the total energy of the respective atoms; allowing such coefficients to vary freely therefore has almost no salutary effect on the description of the atoms themselves but may well lead to a significant improvement in the representation of a molecular environment. This effect is quite apparent in bond formation between atoms and/or small molecular fragments. Its magnitude can be judged, for example, from previous SCF calculations on acetylene in which the fixed group basis and a less restrictively grouped species (2s and 2p groups each decomposed into two parts) is employed;¹⁴ the energy lowerings effected by this added flexibility are seen to increase sharply as bond formation proceeds (Table VI).²⁵ Clearly the choice of basis set is crucial in energy comparisons involving structures with greatly different geometries (such as are necessary in determining heats of formation), but less critical for obtaining

(25) Despite the large magnitude of these changes in energy the calculated equilibrium geometry of such systems is relatively unaffected. Under the assumption that the more flexible basis set's potential curve can be satisfactorily expressed by the quadratic form $\frac{1}{2}k(R - R_0)^2$ and that in the region of the potential minimum the discrepancy in energy between the two basis sets is a linear function with slope A (for example, see Table VI; A is approximately -0.1 hartree/bohr for C_2H_2), the difference in calculated R_0 value is equal to $-A/k$ with the fixed group result the larger. For acetylene this ratio amounts to a difference of only 0.07 bohr.

Table VI. Comparison of SCF Energy Values Obtained from the Fixed Group and the Extended AO Basis Set for C_2H_2 as a Function of Internuclear Distance R_{CC}

R_{CC} , bohrs	ΔE , hartree ^a
2.172	0.0804
2.272	0.0698
2.372	0.0611

^a $\Delta E = E(\text{fixed group basis}) - E(\text{extended basis})$; values from ref 14. $\Delta R_{CC}(\text{equilibrium}) = -A/k > 0$ (see ref 25).

a portion of a potential surface in a fairly localized region.²⁶

Extended Basis Set Calculations

A. SCF Calculations with Extended AO Basis. In order to better judge the effect increased flexibility in the basis set has on the description of the reaction surface for amino additions of olefins, calculations with a more extended basis have been carried out for a series of key nuclear conformations. The new basis is obtained from the former fixed group set in the same way as in the aforementioned treatment of acetylene,¹⁴ that is, by decomposing each of the 2s and 2p groups into a one-component long-range part (smallest exponent of the original group) and a multicomponent group consisting of the remaining primitive Gaussians (with the same contraction coefficients as before); in so doing the number of free coefficients to be determined in the SCF procedure is increased from 24 to 36. Since this extended basis has generally led to much better agreement with experimental data than has the more restricted set, the hybridization factor (see Table II) is redefined for this treatment; the experimental value of R_{CC} is used rather than the calculated one so that $\gamma' = 0.0$ corresponds to $R_{CC} = 1.34$ Å, and $\gamma' = 1.0$ to $R_{CC} = 1.54$ Å. The final C_2NH_6 compound is thus characterized by $\gamma' = 1.0$ and $R_{CN} = 2.78$ bohrs (exptl CN distance for amines) in the extended basis set calculations while values of $\gamma' = 0.0$ and $R_{CN} = 20.0$ bohrs are employed for the reactants. For the transition state the previously determined value of $R_{CN} = 3.8$ bohrs is maintained and $\gamma' = 0.5$ ($R_{CC} = 1.44$ Å) is chosen to complete the characterization of this structure.

The results of these SCF calculations are given in Table VII. Both the N and C states were obtained for the intermediate structure, with their energy values differing by less than 1.0 kcal/mol, thereby indicating that the choice of geometrical parameters for the transition state in this basis is quite satisfactory. As expected the improvement effected by the more flexible basis is

(26) In the case of C_2H_2 with $A = -0.1$ hartree/bohr (see ref 25) discrepancies of 30 kcal/mol and more can be accumulated in the fixed group treatment for R variations in the order of only 1 bohr (0.529 Å).

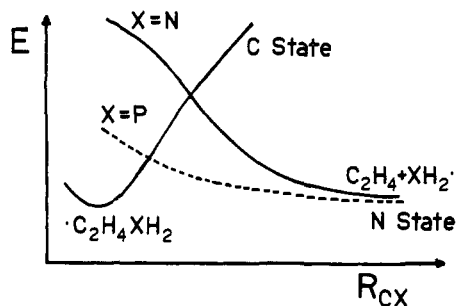


Figure 5. Schematic diagram of the two key states involved in the addition reaction of NH_2 . (Dashed curve for the N state is for attack by PH_2 or amino radicals with electron withdrawing substituents.)

Table VII. Comparison of Energy Values Obtained from Several Calculations Employing the Extended AO Basis^a

	SCF	CI'(9)	CI'(12)
Zero of energy	-133.5282	-133.5659	-133.5805
$\text{C}_2\text{H}_4 + \text{NH}_2\cdot$	0.0	0.0	0.0
Transition state ^b	~36.0	~33.6	~34.6
$\text{C}_2\text{H}_4\text{NH}_2$	-12.5	-6.6	<-5.0 ^c

^a Values in kcal/mol, except for zero of energy, which is in hartrees. ^b Since the assumed transition state geometry may not actually correspond to the energy maximum in the true minimum energy path for the reaction these results can only be considered approximate. ^c CI for combined molecule does not include all excitations whereas the corresponding CI for the separated products does; inclusion of all excitations for both structures would necessarily produce a somewhat lower value than that actually calculated in this case.

significantly more apparent for the combined radical; as a result the heat of formation is lowered to -12.5 kcal/mol, in substantially better agreement with the corresponding experimental value. The activation energy is also considerably reduced compared to its value in the fixed group SCF treatment, although it must be remembered that this result is obtained merely as the difference between the energy of the separated fragments and that of the *assumed* transition state structure.

B. CI Calculations with Extended AO Basis. Just as in the fixed group treatment a CI calculation comparable to the previous CI(6) treatment is necessary in order to obtain the smooth transition between the two states. Doubling the number of 2p AO's at each nuclear center obviously complicates the situation in the present case by increasing the number of MO's composed of in-plane p functions from six to twelve.

A valence set of 12 MO's (all of the same symmetry) leads to a secular equation slightly larger than could be solved with the CI programs at hand, and therefore two different CI calculations have been carried out: one in which only the nine most stable of these 12 MO's are chosen from the valence set [denoted as CI'(9)] and the other, in which all of these 12 MO's are assigned to the valence set but for which various lightly interacting (with the ground state) species are excluded from consideration [denoted as CI'(12)].

The results contained in Table VII indicate a heat of reaction of approximately -6 kcal/mol; this value is still some 11 kcal/mol above the expected experimental heat of reaction (-17 ± 2 kcal/mol).¹⁰ Thus it appears

that even the extended basis is biased toward the more atomic environment, although the effect is clearly smaller in this case than in the fixed group treatment.²⁷ The use of the more flexible AO basis makes the role of the CI less important in the calculation of the heat of reaction; CI with the extended AO basis favors the separated molecules by only 6 kcal/mol, as compared to a value of approximately 13 kcal/mol obtained in the analogous fixed group treatment (Table IV). The smaller of these values is undoubtedly a better estimate for the difference in correlation energy between reactants and product. The present treatment also produces a smaller change between the respective SCF and CI results for the activation energy.

The conclusion emanating from this series of calculations is that the choice of AO basis set is quite important (at least as long as emphasis is put on quantitative reliability) in comparing structures with widely differing nuclear geometries, particular for those interesting cases in which heavy atoms (or molecular fragments which contain only one such atom) come into the bonding region of other molecular systems. The choice of basis set is less critical, however, in treatments of unimolecular reactions in which bonds are broken without drastically altering the environment at any given heavy atom of the system, as has been demonstrated in previous calculations.^{21,22} In addition even in the study of bimolecular reactions a relatively inflexible basis has been seen to be of considerable value in the determination of the approximate structures of various key conformations and, perhaps more importantly, in the elucidation of the essential *qualitative* features governing the course of such reactions.

Conclusion

The calculations of the present paper indicate that the relative inactivity of the amino radical in addition reactions with olefins is caused by a high energy of activation for this process, in the order of 35–40 kcal/mol. The transition state predicted in this study corresponds to a weakened CN bond, approximately 0.5 \AA greater in length than its equilibrium counterpart in the combined $\cdot\text{CH}_2\text{CH}_2\text{NH}_2$ radical. The necessary change in hybridization at the central carbon in the addition process is approximately 60% complete when this structure is formed (as measured in terms of R_{CC} , β_2 , and α_2).

The reaction is best viewed in terms of the crossing between two electronic states (Figure 2a,b): one with a lone pair and an odd electron at the nitrogen atom (most stable for the reactants); the other with a saturated nitrogen atom, a partially formed CN bond, and an odd electron localized at the carbon atom. This crossing is particularly interesting in light of the fact that orbital symmetry is completely conserved in the transition between the two SCF states involved. A schematic diagram of the corresponding two potential curves is given in Figure 5.

These results would also seem to be pertinent to the understanding of certain other experimental observations, particularly those which indicate that both $\text{PH}_2\cdot$

(27) Most of the remaining discrepancy can be removed by the addition of basis functions located *between* the N and central C atoms, thereby favoring the bonding process while having essentially no effect on the representation of the separated reactants.

and $\text{NF}_2\cdot$ are considerably more reactive^{28,29} toward addition than is the simple amino radical. In both $\text{PH}_2\cdot$ and $\text{NF}_2\cdot$ (though for somewhat different reasons) the nonbonding electron density at their respective heavy atoms is expected to be substantially lower than for $\text{NH}_2\cdot$ itself. Consequently the repulsive interaction between the nonbonding electrons of these species and the double bond of the olefinic center is undoubtedly diminished relative to the case of simple amino additions; the resulting decrease in the slope of the N potential curve (Figure 5) quite naturally leads to a reduction in the activation energy for such processes and

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hence to the observed increase in reactivity. This interpretation in turn suggests strongly that the transition state for amino additions is destabilized by electron-donating substituents, in apparent contrast to the behavior of its counterpart in hydrogen abstraction reactions.^{4,5}

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A Kinetic Study of the Proton Hydrate $\text{H}^+(\text{H}_2\text{O})_n$ Equilibria in the Gas Phase

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Abstract: The kinetics of the gas-phase reactions $\text{H}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} + \text{M} = \text{H}^+(\text{H}_2\text{O})_n + \text{M}$ were studied in a pulsed electron beam high pressure mass spectrometer. The major gas used was methane at a few Torr. Some runs were also made with propane. Water pressures were between 1 and 200 mTorr and temperatures up to $\sim 900^\circ\text{K}$ were used. The kinetics of the approach to the equilibria and the equilibria could be observed under these conditions. The rate constants for the forward and reverse reactions of the lower equilibria were determined at different temperatures. The temperature dependence of the equilibrium constants was used for the evaluation of the $\Delta H^\circ_{n-1,n}$ and $\Delta G^\circ_{n-1,n}$. The present results were found to be in fair agreement with earlier determinations from this laboratory but differ drastically with chemical ionization measurements of Beggs and Field.¹

A mass spectrometric study of the ions present in air at near atmospheric pressures (~ 100 Torr) undertaken some 10 years ago led to the accidental observation^{2,3} of the proton hydrates $\text{H}^+(\text{H}_2\text{O})_n$ formed by ion-molecule reactions involving traces of water vapor. The observation of clusters such as $\text{NH}_4^+(\text{NH}_3)_n$, $(\text{H}_2\text{O})_n$, $\text{H}^+(\text{CH}_3\text{OH})_n$, etc., in ammonia, methanol, and other gases led to the systematic study of ion-solvent molecule interactions and ion equilibria in the gas phase.⁴ Measurement of ionic equilibria and their temperature dependence leads to important thermochemical information. For example, determination of the equilibrium constant $K_{n-1,n}$ at suitable temperatures

$$\text{H}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} = \text{H}^+(\text{H}_2\text{O})_n \quad (n-1, n)$$

$$K_{n-1,n} = [\text{H}^+(\text{H}_2\text{O})_n] / [\text{H}^+(\text{H}_2\text{O})_{n-1}][\text{H}_2\text{O}]$$

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(3) Attachment of water molecules to the hydrogen ion had been mass spectrometrically observed earlier in flames [P. F. Knewstubb and T. M. Sugden, *Proc. Roy. Soc., Ser. A*, **255**, 520 (1960)], field emission [H. D. Beckey, *Z. Naturforsch. A*, **15**, 822 (1960)], and gas discharges [P. F. Knewstubb and A. W. Tickner, *J. Chem. Phys.*, **38**, 464 (1963)].

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leads to the determination of $\Delta G^\circ_{n-1,n}$, $\Delta H^\circ_{n-1,n}$, and $\Delta S^\circ_{n-1,n}$ for the stepwise hydration of the proton. Measurement of ion equilibria in the gas phase is useful not only in the study of ion-solvent molecule interactions. The ion-equilibrium method is quite general and has been used in this and other laboratories for the determination of important thermochemical quantities: electron affinities,⁵ switching reaction,⁶ gas-phase acidities and basicities,⁷ H bonding to negative ions,⁸ etc. It is to be expected that future equilibrium measurements will provide a large store of data of fundamental interest to many fields of chemistry. Ion-molecule reaction equilibria are generally observed in the presence of reactions by which the ionic charge is destroyed, *i.e.*, positive-negative charge recombination and discharge by diffusion to the wall. Therefore in order to study ion equilibria one must work under conditions where the equilibrium reactions are faster than the other processes. Also the ion sampling method may create problems. Because of these inherent difficulties,

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