

# Thermochemistry of *trans*-Diimide and 1,1-Diazene. Ab Initio Studies

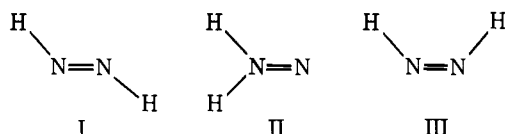
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**Abstract:** The thermochemistry of *trans*-diimide, 1,1-diazene, *cis*-diimide, and diazenyl radical has been obtained using ab initio generalized valence bond and configuration interaction methods. We find the following N-H bond energies at 298 K: *trans*-diimide, 71.5 kcal; 1,1-diazene, 43.0 kcal; diazenyl radical, -24.1 kcal. The results of this study are used to interpret conflicting experimental results and to predict the thermochemistry of substituted 1,1-diazenes.

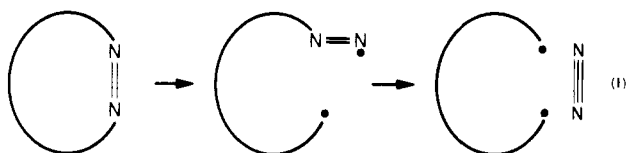
## I. Introduction

The thermochemistry of the isomers of  $N_2H_2$  has been the subject of intense theoretical<sup>1</sup> and experimental<sup>2</sup> interest. Diimide (I, III), generated in situ, is widely used as a reagent



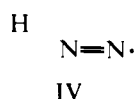
in the stereospecific hydrogenation of double bonds.<sup>3</sup> Although the mechanism of hydrogenation requires *cis*-diimide (III), only *trans*-diimide (I) has been observed spectroscopically.<sup>4</sup> The gas-phase decomposition and reactions of diimide with olefins have also recently been probed by Willis and co-workers.<sup>2a,b,j,k</sup> Despite many studies, I remains a thermochemical enigma, its heat of formation is uncertain, with recent experimental values ranging from 48.7<sup>2d</sup> to 36<sup>2e</sup> to 50.7 kcal,<sup>2f</sup> and its NH bond energy is unknown. Knowledge of this thermochemistry is of particular importance to nitrogenase action, since coordinated I and  $N_2H\cdot$  (IV) have been found in experimental models of nitrogen fixation.<sup>5</sup> 1,1-Diazene (II) has not been observed experimentally, although transition-metal complexes of 1,1-diazene have been well characterized.<sup>5,6</sup> GVB-CI (generalized valence bond-configuration interaction) calculations show that the ground state of II is a singlet<sup>7</sup> (earlier theoretical studies<sup>1a,m</sup> had indicated a triplet). Recently, a dialkyl-substituted diazene (often proposed as a reaction intermediate)<sup>8</sup> has been isolated and characterized by Hinsberg and Dervan,<sup>9</sup> leading to vibrational frequency and electronic excitation consistent with the GVB calculations on the parent diazene.

An important current problem concerning diazenes is the question of stepwise decomposition (1) vs. simultaneous fission



of both bonds.<sup>10</sup> Such considerations would be aided by knowledge of the energetics, even for the  $R = H$  case.

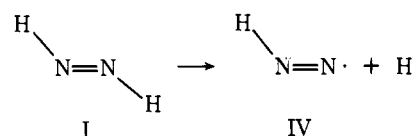
This paper will present the results of GVB-CI studies on the thermochemistry of *trans*-diimide, *cis*-diimide, and 1,1-diazene and their common decomposition product, the diazenyl radical (IV).



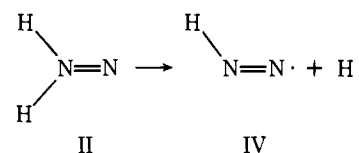
## II. Results and Discussion

The details of the calculation are described in section IV. Here we summarize the results and discuss the implications. Our studies lead to<sup>1a</sup>

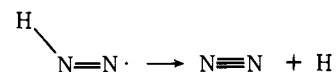
(i)  $\Delta H_0 = 70.0$  kcal and  $\Delta H_{298} = 71.5$  kcal for



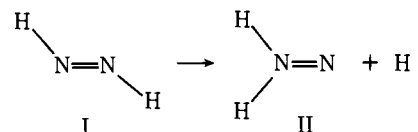
(ii)  $\Delta H_0 = 41.5$  kcal and  $\Delta H_{298} = 43.0$  kcal for



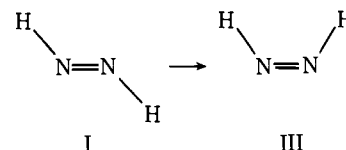
(iii)  $\Delta H_0 = -25.3$  kcal and  $\Delta H_{298} = -24.1$  kcal for



(iv)  $\Delta H_0 = \Delta H_{298} = 27.4$  kcal for

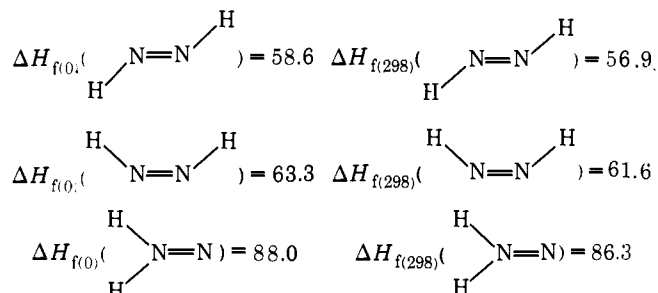


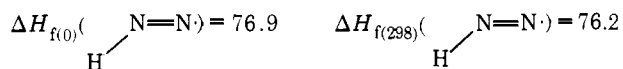
(v)  $\Delta H_0 = \Delta H_{298} = 4.7$  kcal for



where  $\Delta H_0$  and  $\Delta H_{298}$  are the enthalpy values at 0 and 298 K, respectively.

From these studies we find the following heats of formation:





Experimental values of  $\Delta H_{f(298)}$  for *trans*-diimide are  $48.7 \pm 5$  (1958),<sup>2d</sup>  $36 \pm 2$  (1976),<sup>2e</sup> and  $50.7 \pm 2$  kcal (1978).<sup>2f</sup> The latter two values differ by 15 kcal, although the uncertainties are only 2 kcal. Our value of 56.9 kcal strongly supports this latest value for the heat of formation for *trans*-diimide.

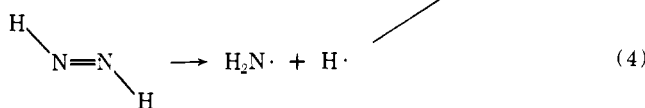
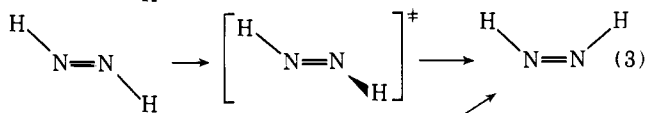
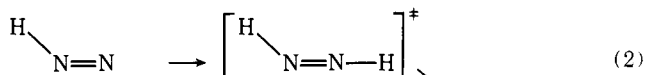
Direct calculations predict that *cis*-diimide is 4.7 kcal higher in energy than *trans*-diimide. This is in contradiction to Wiberg's claim<sup>2h</sup> that the two isomers are of approximately equal energies.

The  $\Delta H_{f(0)}$  of 88.0 kcal calculated here for 1,1-diazene (II) is in excellent agreement with the GVB-CI value of 88.4 kcal calculated by Davis and Goddard.<sup>7</sup>

Direct calculations put the 1,1-diazene (II) higher in energy than the 1,2-diazene (I) by 27.4 kcal (298 K).<sup>11</sup> Appearance-potential measurements by Wiberg et al. have been interpreted in terms of the 1,1-diazene lying only 13 kcal above the 1,2-diazene.<sup>2i</sup> Our results are in strong disagreement with this interpretation of the experiments.

Experimental NH bond energies of I, II, and III are unknown. The calculated energies of 71.5, 42.0, and 66.8 kcal (298 K) for I, II, and III, respectively, indicate that the diazenes should be stable to NH cleavage.

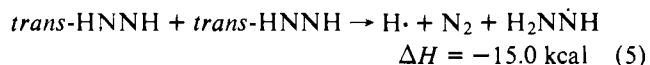
The first step in the gas-phase reactions of diimide is thought to be the rate-controlling isomerization of I  $\rightarrow$  III.<sup>2j</sup> Recently an experimental activation energy of 4.2 kcal for this process has been reported.<sup>2j</sup> The mechanism and barrier to isomerization have stimulated many theoretical enquiries. Three mechanisms for this isomerization (eq 2-4) have recently been



investigated.<sup>1a,b,d-i,k</sup> Previous calculations have shown that the inversion mechanism (2) is favored over rotation (3).<sup>1a,f,h,i</sup> Inversion barriers cluster around 46-51 kcal,<sup>1a,b,d-i,k</sup> whereas rotation barriers are in the range of 55-84 kcal.<sup>1a,f,h,i</sup> Pasto and Chipman<sup>1d</sup> have recently compared the activation energies for (2) and (4); they calculate 46.2 kcal for (4) and 46.0 kcal for (2) but estimate that correlation effects would increase (4) to 66-76 kcal. We find that the dissociation-recombination pathway (4) has an activation energy of 71.5 kcal;<sup>12</sup> therefore, this pathway to isomerization can be ruled out.

None of these isomerization pathways is consistent with the 4.2 kcal barrier to *trans*-diimide decomposition observed by Willis and co-workers.<sup>2j</sup> (Interestingly, the experimental barrier is almost identical with the 4.7 kcal calculated energy gap between the isomers.) For this reason we propose a radical-chain mechanism for the observed *trans*-*cis* isomerization. Using the thermochemistry developed in this work, and the experimental heats of formation of hydrazine<sup>13a</sup> ( $\Delta H_{f(298)} = 22.8$  kcal/mol) and of hydrazyl radical<sup>13b</sup> ( $\Delta H_{f(298)} = 46.7$  kcal/mol), the radical mechanism and its thermochemistry are outlined below.

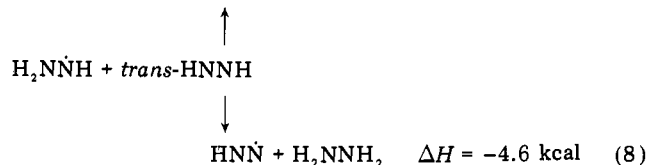
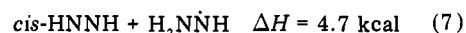
The initiation step is



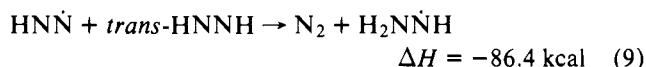
a reaction first suggested by Wiberg to account for the disproportionation of I to nitrogen and hydrazine.<sup>2i</sup> This process is calculated to be downhill by 15 kcal. The hydrogen radical may then react exothermically with *trans*-diimide to form another hydrazyl radical:



The hydrazyl radical formed directly in (5) or indirectly in (6) may react with *trans*-diimide either to form *cis*-diimide or diazenyl radical and hydrazine:



The diazenyl radical can regenerate hydrazyl radical via another highly exothermic reaction:



Or, alternately, it may decompose directly to give H $\cdot$ , which can carry on the chain as in (6):



The experimentally observed activation energy for *trans*-diimide decomposition of 4.2 kcal<sup>2j</sup> is consistent with a radical-chain mechanism, with (7) as the rate-determining step.

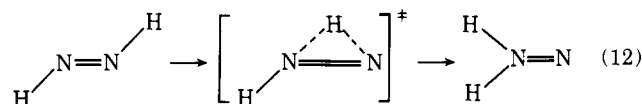
The radical disproportionation reaction



has been examined by Pasto<sup>10</sup> by SCF calculations and found to be exothermic by 9.7 kcal. In contrast, we calculate this reaction to be endothermic by 9.1 kcal. Thus, such a reaction is unfavored in diimide reactions.

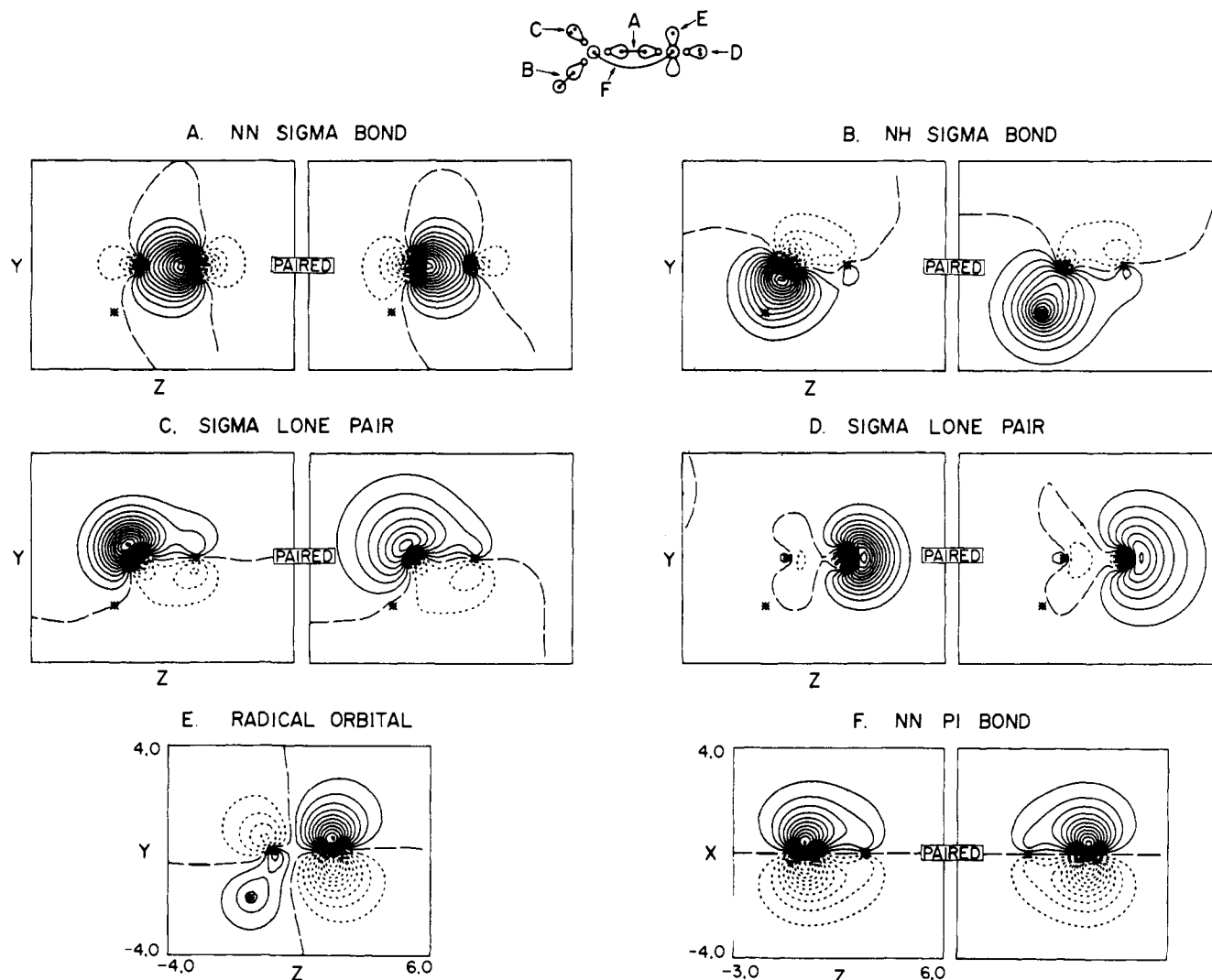
Although the work of Willis and co-workers<sup>2a</sup> rules out a radical-chain mechanism operating in the gas-phase hydrogenation of olefins by diimide, a radical mechanism for the isomerization of *trans*- to *cis*-diimide cannot be excluded. The observation by Willis and co-workers<sup>2k</sup> that the thermal decomposition of *trans*-diimide gives products different from photochemical decomposition does not rule out a different radical chain in the thermal decomposition of *trans*-diimide. We suggest that labeling experiments with deuterated and undeuterated diimide be carried out. A simple unimolecular isomerization mechanism would predict no scrambling of the label, whereas the radical mechanism would.

Recently a great deal of theoretical attention has been focused on the barrier to the rearrangement (12). The barriers



(with no zero-point correction) for the isomerization of I  $\rightarrow$  II have been calculated to be 82.6,<sup>1b</sup> 83.0,<sup>1c</sup> and 87.7<sup>1d</sup> kcal. Since our results indicate a bond energy of 71 kcal, such an isomerization should occur more readily by a dissociation-recombination pathway.<sup>12</sup>

Breaking an N-H bond of I or II results in the formation of diazenyl radical (IV). Although IV has never been experimentally observed, <sup>15</sup>N CIDNP evidence points to the existence of substituted diazenyl radicals in the thermolysis of some azo compounds,<sup>10e</sup> and aryldiazenyl radicals have been invoked as intermediates in many aryldiazonium reactions.<sup>13c</sup> The



**Figure 1.** The GVB orbitals for diazenyl radical  $\text{HN}_2$ . The molecule is in the  $YZ$  plane. Long dashes indicate nodal planes, solid lines indicate positive amplitude, and short dashes indicate negative amplitude. The spacing between contours is 0.05 au.

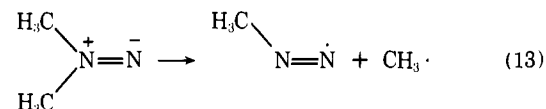
stability of diazenyl radicals is a large factor in determining the mechanism of azo-compound decomposition. For these reasons, the electronic structure of the parent diazenyl radical is of interest. The geometry-optimized GVB orbitals of IV are shown in Figure 1. The conjugative delocalization of the nitrogen lone pair onto the radical center confers considerable stability to the diazenyl radical.<sup>14</sup> The three-electron bond also manifests itself in the opening of the  $\text{NNH}$  angle ( $115^\circ$ ) in diazenyl radical relative to the  $\text{NNH}$  angle ( $107^\circ$ ) in *trans*-diimide. The radical delocalization also shortens the  $\text{NN}$  bond by  $0.04 \text{ \AA}$  (from  $1.25 \text{ \AA}$  in I to  $1.21 \text{ \AA}$  in IV). The influence of this three-electron bond is felt in the low barrier to  $\text{N-H}$  inversion in IV (about 34 kcal), which is 13–26 kcal lower than for diimide (I).<sup>1a,b,d-i,k</sup>

The  $\text{NH}$  bond energy of I (71.5 kcal) is much lower than the  $\text{NH}$  bond energy of  $\text{NH}_3$  (106 kcal) owing to the stabilization of the diazenyl radical by an adjacent lone pair, but is similar to the  $\text{NH}$  bond energy of hydrazine (76 kcal) because the hydrazyl radical is also stabilized by a three-electron  $\text{N-N}$  bond.

The  $\text{NH}$  bond energy (at 298 K) of IV was calculated to be  $-24.1 \text{ kcal}$ .<sup>15</sup> The negative value indicates that decomposition of the radical is exothermic; however, there may be a large barrier to bond breaking. Recently, an experimental estimate of a 13-kcal barrier to decomposition has been reported,<sup>2k</sup> in agreement with calculated barriers of 10–20 kcal.<sup>16</sup>

The calculated  $\text{NH}$  bond energy of 1,1-diazene may be used

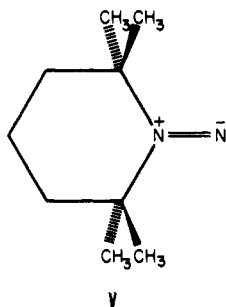
to give a crude estimate of alkyl–nitrogen bond strengths in substituted 1,1-diazenes. Early experimental work by McBride and Kruse<sup>17</sup> has set a lower limit on the activation energy for process 13 of 17 kcal. Correcting the  $\text{NH}$  bond energy of 1,1-diazene by the energy difference between an  $\text{N-CH}_3$  and an  $\text{N-H}$  bond (18.5 kcal)<sup>18,19</sup> we predict that (13) is endo-



thermic by 23.5 kcal at 298 K. This estimate predicts that the activation energy for the first step in the stepwise decomposition of alkyl-1,1-diazenes should be about 24 kcal. Further alkyl substitution and ring strain should lower this number. After completion of this theoretical work, an experimental estimate of 16.9–20.0 kcal was obtained by Hinsberg and Dervan from studies of the decomposition of V.<sup>20</sup> In different solvents, activation energies of 16.9, 20.0, and 20.1 kcal were obtained, in good agreement with our theoretical result, 23.5 kcal.

### III. Comparison with Other Calculations

We find that inclusion of electron correlation is important in calculating the heat of formation of I. For example, Hartree-Fock (HF) calculations using the same basis set and ge-



ometry yield a  $\Delta H_{f(298)}$  for I about 20 kcal too high; see Table I.

Baird and Kathpal<sup>16</sup> and Pasto and Chipman<sup>1d</sup> have carried out HF (4-31G) calculations on the NH bond energy of I, giving energies of 50.0 and 46.2 kcal, respectively. These values are in reasonable agreement with our HF bond energy of 53.2 kcal but much smaller than the value of 71.5 kcal from correlated wave functions.

Pasto and Chipman<sup>1d</sup> have also carried out HF calculations on the NH bond energy of II. Their 40.0-kcal result is in good agreement with our HF result of 35.4 kcal and with the value of 43.0 kcal from correlated wave functions.

Several recent calculations have reported the energy difference between I and II.<sup>21</sup> Extensive, large basis set calculations are in excellent agreement with the GVB-CI result of 27.4 kcal at 298 K. Pople and co-workers,<sup>1c</sup> using a 6-31G\* basis and MP4(SDQ), obtained 25.4 kcal (24.4 kcal at 298 K) for the energy difference. Dykstra,<sup>1b</sup> using the SCEP method with a TZ + 2P basis set, finds 24.5 kcal (23.5 at 298 K). PNO and CEPA calculations of Ahlrichs and Staemmler<sup>1a</sup> predict gaps of 24.0 and 26.0 kcal, respectively. The lower CI result of 20.3 kcal by Baird and Wernet<sup>1j</sup> is probably a reflection of the smaller (4-31G) basis set. Reported HF separations of 17–20 kcal<sup>1b,c,m</sup> are in agreement with the present HF result of 17.8 kcal. The very low 6.0-kcal gap recently predicted by Pasto and Chipman<sup>1d</sup> is a consequence of the lack of polarization functions.<sup>21</sup>

Many theoretical studies have addressed the energy difference between *cis*- and *trans*-diimide. Energy gaps have ranged from a high of almost 13 kcal<sup>1n</sup> to a low of 3.6 kcal.<sup>1p</sup> However, recent large basis CI<sup>1a,b</sup> or perturbation<sup>1c</sup> calculations give energy separations that are extremely close to each other (7.2–5.8 kcal). The GVB-CI calculation of 5.6 kcal is in agreement with the latest values.

A few studies have been directed at the diazenyl radical.<sup>16</sup> Baird<sup>16a</sup> has optimized the geometry of IV and found the  $R_{NN} = 1.18 \text{ \AA}$ ,  $R_{NH} = 1.02 \text{ \AA}$ , and  $\angle HNN = 118^\circ$ , in good agreement with our optimized geometry of  $R_{NN} = 1.21 \text{ \AA}$ ,  $R_{NH} = 1.05 \text{ \AA}$ , and  $\angle HNN = 115^\circ$ . Baird<sup>16a</sup> has also calculated the bond energy of IV at the HF level (4-31G). His value of -9 kcal is in agreement with the present HF result of -12 kcal but differs from the value of -24.1 kcal obtained with correlated wave functions.

#### IV. Computational Details

**Basis Set.** For all calculations the Dunning<sup>22</sup> valence double  $\zeta$  Gaussian basis set was used. This basis was augmented by a set of d polarization functions ( $\alpha = 0.8$ ) on each nitrogen and a set of p polarization functions ( $\alpha = 1.0$ ) on each hydrogen.

**GVB Calculations.** To calculate the NH bond energies of I and II, the NH bond being broken on I and II was described by five natural orbitals, and the remaining valence electron pairs were described by two natural orbitals apiece. IV was described by a wave function in which two natural orbitals were included for each pair of valence electrons, and the radical was described by one orbital.

**Table I.** Theoretical Calculations on the Heat of Formation of *trans*-Diimide (kcal/mol)

method	basis	$\Delta H_f^a$	$\Delta H_{f(298)}$	ref
HF	EXT + POL	48.6	54.3	1e
HF	EXT + POL	71.8	77.5	1a
HF	EXT + POL	68.8	74.5	this work
CI	4-31G	66.0	71.7	1j
CEPA	EXT + POL	49.9	55.6	1a
GVB-CI	EXT + POL	51.2	56.9	this work

<sup>a</sup> No temperature or zero-point correction applied.

To calculate the NH bond energy of IV, this radical was described by allowing two NOs for each valence pair, and the molecular nitrogen was described by a wave function in which each valence pair was described by two natural orbitals.

In order to determine the energy difference among I, II, and III, two natural orbitals were included for each valence pair.

The geometry of IV was optimized by describing the NH bond, the NN  $\pi$  bond, and the NN  $\sigma$  bond with three natural orbitals apiece.

**GVB-CI Calculations.** Harding and Goddard<sup>23</sup> have shown that reliable bond energies for  $\sigma$  bonds are obtainable by partitioning the electrons into an active set, a semiactive set, and an inactive set and then carrying out high-order excitations involving the active set, allowing simultaneous low-order excitations in the semiactive set and no excitations in the inactive set. The active set includes electrons directly affected by the bond-breaking process, the semiactive set includes all electrons adjacent to the active electrons but not intimately involved with the bonding electrons or the resulting radical electron, and finally, for our cases, the only inactive electrons are the nitrogen 1s core electrons. This overall process is referred to as correlation-consistent CI. The level of CI in the semiactive space depends upon the geometric and orbital changes involved in the bond fission; for example, since shortening of the N-N bond is observed after N-H cleavage of I and II due to formation of the three-electron bond in the radical, the N-N  $\sigma$  and  $\pi$  space must be sufficiently correlated in the diazenes and in IV. The semiactive space in this case consists of the full GVB-PP wave function<sup>23f</sup> for the NN  $\sigma$  and  $\pi$  bonds and also includes the N-N  $\sigma$ - $\pi$  interpair terms.<sup>23g</sup> For both of the first bond-breaking processes, section II (i) and (ii), the excitations (full CI) in the active space (the N-H bond consisting of five natural orbitals) are multiplied by the previously mentioned excitations in the semiactive space, and finally strong orthogonality<sup>23f</sup> constraints are removed allowing all single excitations among the active and semiactive electrons from the full product list of configurations, resulting in a subset of quintuple excitations.

The isomerization process, section II (iv) and (v), is easily determined through a CI consisting of an R-CI<sup>23c</sup> limited to triples, with a final strong orthogonality breakdown level of single excitations among the six valence pairs of electrons, each pair of electrons utilizing two natural orbitals. The geometry of the diazenyl radical (IV) is determined in an analogous manner, limiting the active space to the NN  $\sigma$  and  $\pi$  bonds and the N-H  $\sigma$  bond and utilizing three natural orbitals for each of the pairs of electrons.

As opposed to the above relatively straightforward calculations, the bond-breaking process, section II (iii), is conceptually rather difficult since considerable electronic shuffling occurs as the N-H  $\sigma$  bond is broken. The nitrogen electron initially bonded to hydrogen recouples with the radical orbital, forming one of the  $\pi$  bonds of dinitrogen, and one  $\sigma$  lone pair (Figure 1C) rehybridizes, becoming equivalent to the other lone pair (Figure 1D) after the bond has been broken; thus the active space for diazenyl radical must include all five of these

**Table II.** Total Energies (hartrees) and Numbers of Spin Eigenfunctions (NSEF) for Various Calculations

	total energy			NSEF	
	I	II	IV	I, II	IV
HF	-110.020 50	-109.992 09	-109.436 55	1	1
GVB-PP	-110.139 80	-110.091 44	-109.517 22	160	32
GVB-CI	-110.149 14	-110.100 72	-109.533 03	3389	1070

	total energy		NSEF	
	IV	N <sub>2</sub>	IV	N <sub>2</sub>
HF	-109.436 55	-108.958 04	1	1
GVB-PP	-109.517 22	-109.044 62	32	32
GVB-CI	-109.583 23	-109.115 86	6779	1049

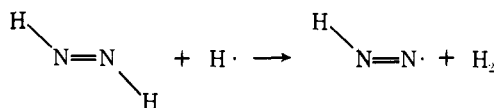
  

	total energy			NSEF
	I	II	III	
HF	-110.020 50	-109.992 09	-110.010 36	1
GVB-PP	-110.130 97	-110.082 67	-110.121 40	64
GVB-CI	-110.193 28	-110.147 97	-110.184 40	3548

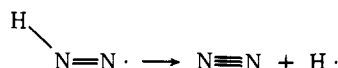
electrons, which implies that for dinitrogen one lone pair and one  $\pi$  bond are included in the active space; the remaining valence electrons are contained in the semiactive space. For this calculation, the active space excitations are limited to RCI triples (plus doubles and singles), followed by singles to allow breakdown of strong orthogonality. This active list of configurations is multiplied by RCI triples in the semiactive space, and finally strong orthogonality constraints are removed in the full space (active plus semiactive).

**Geometry.** The experimental geometry<sup>24</sup> of *trans*-diimide was used in all calculations of I. The partially optimized geometry of Davis and Goddard<sup>7</sup> was used in the calculations of II. The optimized geometry of Parsons and Dykstra<sup>1b</sup> was used in calculations of III. The geometry of the diazenyl radical was fully optimized at the GVB-CI level, giving NN = 1.209 Å, NH = 1.053 Å, and NNH = 114.6°.

**Retention of Bondedness.** Accurate bond energies require inclusion of those electron correlation effects that are modified by the process of breaking the bond. Thus, to obtain the most accurate bond energies at a given level of correlation, it is useful to consider processes involving formation and dissolution of similar bonds. For example, in place of process (i) of section II, we use



On the other hand, for process (iii) of section II



an NH  $\sigma$  bond is broken while an NN  $\pi$  bond is formed, and no modification in the process is made.

By considering processes with constant bondedness, even HF calculations can yield moderately reliable bond energies.<sup>25</sup> However, since HF leads to much larger correlation errors in  $\pi$  bonds than in  $\sigma$  bonds, processes that change the number of  $\sigma$  and  $\pi$  bonds may lead to larger errors for HF.

**Zero Point Energy Corrections.** In order to calculate enthalpies at 0 K we must add the zero-point energy to the

calculated energies. The 1,1-diazene zero-point energy of 16.2 kcal used in these calculations was estimated by Davis and Goddard.<sup>7</sup> The diazenyl radical (IV) zero-point correction is estimated to be 8.7 kcal by estimating fundamental frequencies (N-H stretch = 3130, HNN bend = 1434, NN stretch = 1529  $\text{cm}^{-1}$ ). The zero-point energy of 17.2 kcal for I was calculated using the five experimentally known<sup>24,26</sup> fundamental frequencies of vibration [NH stretch ( $a_g$ ) = 3128, NNH bend ( $a_g$ ) = 1583, NN stretch ( $a_g$ ) = 1529, NH stretch ( $b_u$ ) = 3120, and NNH bend ( $b_u$ ) = 1286  $\text{cm}^{-1}$ ] and estimating the unknown torsional frequency to be 1350  $\text{cm}^{-1}$ . The zero-point energy correction for *cis*-diimide (III) of 16.7 kcal is calculated by estimating fundamental frequencies of vibration [NH stretch = 2994,<sup>4</sup> NN stretch = 1529, NNH bend = 1587, NH stretch = 2956,<sup>4</sup> NNH bend = 1290, and torsional = 1350  $\text{cm}^{-1}$ ]. The zero-point corrections for N<sub>2</sub> and H<sub>2</sub> are 3.4 and 6.3 kcal, respectively.

**Temperature Corrections.** In order to calculate enthalpy changes at 298 K, we must correct the 0 K results. In doing this we assumed a constant  $C_p$  of 8 cal/deg for I, II, and IV, 5 cal/deg for H, and 7 cal/deg for N<sub>2</sub> and H<sub>2</sub>.

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## A Palladium-Catalyzed Reaction of a $\pi$ -Allyl Ligand with a Nucleophile. An MO Study about a Feature of the Reaction and a Ligand Effect on the Reactivity

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**Abstract:** A CNDO-type MO study was carried out for the reaction between OH<sup>-</sup> and the  $\pi$ -allyl ligand coordinating to palladium(II), as a model reaction of various nucleophilic attacks on the  $\pi$ -allyl ligand. MO calculations showed the following feature of the reaction: when a nucleophile, Y, approaches the  $\pi$ -allyl ligand, the palladium(II) is reduced to palladium(0), and the  $\pi$ -allyl ligand is eliminated as an allyl derivative, CH<sub>2</sub>=CHCH<sub>2</sub>Y, from the palladium(0). This feature agrees with the experimental result. The reactivity regarding the OH<sup>-</sup> nucleophilic attack increases in the order PdCl<sub>2</sub>( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sup>-</sup>  $\ll$  PdCl(PH<sub>3</sub>)( $\pi$ -C<sub>3</sub>H<sub>5</sub>) (B) < PdCl(PH<sub>3</sub>)( $\pi$ -C<sub>3</sub>H<sub>5</sub>) (A)  $\sim$  [PdCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> < PdCl(CO)( $\pi$ -C<sub>3</sub>H<sub>5</sub>) (B) < PdCl(CO)( $\pi$ -C<sub>3</sub>H<sub>5</sub>) (A) < Pd(PH<sub>3</sub>)<sub>2</sub>( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sup>+</sup> (B) < Pd(PH<sub>3</sub>)<sub>2</sub>( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sup>+</sup> (A), where (A) indicates an inclusion of the Pd 4d $\pi$ -CO  $\pi^*$   $\pi$ -acceptor interaction in PdCl(CO)( $\pi$ -C<sub>3</sub>H<sub>5</sub>) and inclusion of the Pd 4d $\pi$ -P 3d $\pi$  interaction in PdCl(PH<sub>3</sub>)( $\pi$ -C<sub>3</sub>H<sub>5</sub>) and Pd(PH<sub>3</sub>)<sub>2</sub>( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sup>+</sup>, and (B) indicates exclusion of the interactions. Although the anionic ligand is unfavorable for the reaction, the neutral  $\pi$ -acceptor ligand is favorable. MO calculations support the proposal of Trost et al. that the nucleophilic attack of the carbanion on the  $\pi$ -allyl ligand is accelerated by addition of triphenylphosphine, and that the cationic complex, Pd(PPh<sub>3</sub>)<sub>2</sub>( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sup>+</sup>, is an active intermediate. It is discussed why the neutral  $\pi$ -acceptor ligand is favorable for the nucleophilic reaction and why the anionic ligand is unfavorable.

### Introduction

It has been known that palladium complexes act as catalysts of various kinds of reactions such as the Wacker reaction, the isomerization and hydrogenation of alkenes, and nucleophilic attack on alkene and  $\pi$ -allyl ligands coordinating to palladium(II).<sup>1-3</sup> The nucleophilic attack on the ligand seems an important characteristic of the palladium catalysis, because various nucleophilic reactions of carbanion, amine, acetate anion, etc., are considered useful in the field of organic synthesis.<sup>4-17</sup> A nucleophilic reaction of a carbanion with the  $\pi$ -allyl ligand has been actively studied from the viewpoint of a formation of a new C-C bond,<sup>4,6,10,14-17</sup> and it has been noted that addition of a tertiary phosphine greatly accelerates the nucleophilic attack.<sup>9,16a</sup>

Although many experimental studies have been reported

as described above, no theoretical work has been performed on such a nucleophilic reaction. The theoretical work can characterize a feature of the reaction and can elucidate why the tertiary phosphine accelerates the reaction. Knowledge about these issues seems necessary to advance the study of palladium catalysis. In this work, CNDO-type semiempirical SCF-MO calculations were carried out on some  $\pi$ -allylpalladium complexes, PdCl<sub>2</sub>( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sup>-</sup>, PdCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>) (L = CO or PH<sub>3</sub>), [PdCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub>, and Pd(PH<sub>3</sub>)<sub>2</sub>( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sup>+</sup>, and on a reaction between the OH<sup>-</sup> and the  $\pi$ -allyl ligand in the above complexes. Although the OH<sup>-</sup> has not been known to react with the  $\pi$ -allyl ligand to form allyl alcohol, the OH<sup>-</sup> is considered here as a model of a usual nucleophile such as phenoxide, acetate, carbanion, etc. The purpose of this work is twofold; first, to elucidate how the electronic structure of the palladium complex is changed by the nucleophilic attack;