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Theoretical Study of the Kinetic Barriers in Dihydrogen-Exchange Reactions

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Abstract: Ab initio calculations have been performed on the transition structures for the symmetrical dihydrogen-exchange reactions between *cis*-N_2H_2 and N_2, N_2H_4 and *trans*-N_2H_2, C_2H_4 and C_2H_2, and C_2H_6 and C_2H_4. At the HF/6-31G* level, concerted orbital-symmetry-allowed pericyclic transition structures were located for all four reactions. At the MP2/6-31G* level, similar transition structures were located for all reactions except that of N_2H_4 with N_2H_2, where a double-saddle point was found. At this level the N_2H_4/N_2H_2 reaction also displayed a very shallow local potential energy minimum corresponding to sequential H-atom transfer; however, enthalpies calculated at all levels for this reaction strongly suggested the mechanism to be concerted. For all four reactions, activation energies calculated at the MP2 level were much less than those calculated at the HF level but still significant. Calculations at the MP4/6-31+G(2d,p)//MP2/6-31G* level led to values for $\Delta H^{\ddagger}$ of about 20 kcal/mol for the nitrogen compounds and about 50 kcal/mol for the carbon compounds. These results show that the activation energies are highly sensitive to the electronegativity of the central atoms but not to the bond order. It is suggested that, with proper reagent design, concerted thermoneutral dihydrogen transfer could occur with a rather low activation energy.

Introduction

Hydrogenation and dehydrogenation of molecules constitute an important class of chemical reactions. These reactions can occur in various ways, including polar, free radical, and catalyzed mechanisms. Our recent interest, however, has focused on the symmetry-allowed concerted transfer of a pair of vicinal hydrogen atoms from one moiety to another. The fundamental problem is to understand the nature of the kinetic barriers to these reactions. Such reactions have proven difficult to study experimentally, and until recently the computational costs have been so high that some of the most basic features of the reactions have escaped detection.

The most widely-recognized group of concerted dihydrogen-transfer reactions is that where 1,2-diazene (N_2H_2) donates its hydrogen atoms to olefins, acetylenes, and azo compounds.[1] These reactions have long been understood to have pericyclic mechanisms, the primary evidence being their stereospecificity. Recently one of us presented the first experimental determination of the bimolecular rate constants for two such reactions: 2.0×10^4 M^{-1} s^{-1} and 1.4×10^3 M^{-1} s^{-1} for the aqueous reactions of N_2H_2 with itself and azobenzene-4,4′-disulfonate, respectively.[2] These reactions have very large driving forces. The other class of concerted dihydrogen-transfer reactions for which kinetic data are available involves intramolecular transfer from a saturated >CH–CH< group to an olefinic group and is known as dyotropic rearrangement.[3] Mackenzie et al. have obtained activation parameters for a series of such reactions in which the dihydrogen donor group becomes part of an aromatic system, and hence the reactions have substantial driving forces.[4] Essentially thermoneutral dyotropic rearrangements have been examined by Hagenbuch et al. and Paquette et al.[5,6] These dyotropic rearrangements have activation enthalpies ranging from 24 to 39 kcal/mol and also have substantial entropic barriers. One immediate question posed by these observations is the following. Why do the reactions with N_2H_2 as the donor have such small barriers when compared to the reactions with >CH–CH< groups as donors?

There have been several computational studies of concerted dihydrogen transfer. These include reactions with *cis*-N_2H_2 as a donor[7-13] and the reaction of C_2H_6 with C_2H_4.[14] Our recent study of the reactions of *cis*-N_2H_2 showed that meaningful results could only be obtained when the effects of electron correlation were included.[13] When these effects were taken into account, it was found that dihydrogen donations from *cis*-N_2H_2 to *cis*-N_2H_2, *trans*-N_2H_2, and C_2H_4 had activation enthalpies effectively equal to zero and that the calculated activation entropies were sufficient to account for the experimentally-determined rate constants. In the study of the C_2H_6 exchange reaction with C_2H_4, a barrier of 71 kcal/mol was calculated.[14] Although this result is much higher than the experimentally-observed activation enthalpies for dyotropic rearrangements, both the calculated and observed barriers are quite large.

In summary, the experimental and computational results are now in good agreement that concerted dihydrogen transfer from *cis*-N_2H_2 is a facile process but that the analogous process from a saturated >CH–CH< group is kinetically quite hindered. Whether this difference reflects the greater driving force for reactions of N_2H_2, whether it is due to the difference between double bond/triple bond or single bond/double bond systems, or whether it is due to an intrinsic difference between nitrogen and carbon chemistry is the subject of the present paper.

Method of Calculation

All calculations were performed by using the GAUSSIAN88 program package[15] with the RHF technique except for the open-shelled cases of N_2H_3 and N_2H where the UHF technique was used. Geometries were fully optimized within the appropriate point group at the HF/6-31G* and MP2/6-31G* levels.[16] Transition structures for the symmetrical di-

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Table I. Calculated Energies and Entropies of the Molecules, Complexes, and Transition Structure[a]

		//6-31G*		//MP2/6-31G*				
		6-31G*[b]	MP4/ 6-31G*	MP2/ 6-31G*	MP4/ 6-311G**	MP4/ 6-31+G(2d,p)	ZPE[b]	S
N_2[c]	$D_{\infty h}$	−108.943 95 (0)	−109.266 49	−109.261 57	−109.316 16	−109.305 17	3.12 (0)	45.87
N_2H[c]	C_s	−109.425 40 (0)	−109.745 12	−109.724 39	−109.797 26	−109.788 36	9.82 (0)	53.47
N_2H_3	C_1	−110.570 28 (0)	−110.902 80	−110.880 99	−110.980 56	−110.973 74	25.51 (0)	56.51
trans-N_2H_2[c]	C_{2h}	−109.994 76 (0)	−110.338 66	−110.321 52	−110.407 50	−110.398 71	17.91 (0)	52.19
cis-N_2H_2[c]	C_{2v}	−109.983 50 (0)	−110.328 98	−110.311 07	−110.397 38	−110.389 34	17.47 (0)	52.23
N_2H_4[c]	C_2	−111.169 37 (0)	−111.525 61	−111.504 40	−111.617 06	−111.610 00	34.33 (0)	55.00
C_2H_2[c]	$D_{\infty h}$	−76.817 83 (0)	−77.091 11	−77.076 22	−77.139 94	−77.133 64	16.22 (0)	49.08
C_2H_4[c]	D_{2h}	−78.031 72 (0)	−78.318 70	−78.294 29	−78.382 39	−78.376 79	32.68 (0)	52.31
C_2H_6[c]	D_{3d}	−79.228 76 (0)	−79.532 34	−79.503 97	−79.614 52	−79.605 22	48.45 (0)	54.20
$N_4H_2(TS_1)$	D_{2h}	−218.828 36 (1)	−219.551 47	−219.541 53	−219.679 52	−219.656 41	18.45 (1)	61.32
$N_4H_6(TS_2)$	C_{2h}	−221.057 11 (1)	−221.821 99	−221.798 71	−221.991 49	−221.970 16	49.70 (2)	64.80
$N_4H_6(SS_2)$	C_i			−221.799 21	−221.990 77	−221.971 07	52.71 (0)	68.82
$C_4H_6(TS_3)$	D_{2h}	−154.705 90 (1)	−155.312 18	−155.283 45	−155.433 71	−155.419 83	46.64 (1)	64.15
$C_4H_{10}(TS_4)$	D_{2h}	−157.131 94 (1)	−157.762 45	−157.718 02	−157.917 64	−157.899 91	78.65 (1)	67.43

[a] Electronic energies in hartrees, (1 hartree = 627.49 kcal/mol). ZPE in kcal/mol. MP2 correlation energies calculated with core electrons included; MP4 correlation energies calculated with frozen core approximation. S in cal K^{-1} mol^{-1} at 298 K and 1 atm. ZPE and S calculated at the MP2/6-31G* level. [b] Parenthetical number is the number of imaginary vibrational frequencies. [c] From ref 13, which also includes Z-matrices for these species.

Table II. Energy and Entropy Changes in the Free Radical Reactions[a]

	//6-31G*		//MP2/6-31G*					
	6-31G*	MP4/ 6-31G*	MP2/ 6-31G*	MP4/ 6-311G**	MP4/ 6-31+G(2d,p)	ΔH°	ΔS°	ΔG°
N_2 + *cis*-$N_2H_2 \rightarrow 2N_2H$	48.1	66.0	77.7	74.7	73.9	73.3	8.8	70.7
trans-$N_2H_2 + N_2H_4 \rightarrow 2N_2H_3$	14.8	36.8	40.1	39.8	38.4	36.1	5.8	34.4

[a] Energies in kcal/mol, and ΔS° in cal K^{-1} mol^{-1}. ΔG°, ΔH°, and ΔS° at 298 K and 1 atm.

Table III. Activation Parameters in the Degenerate Dihydrogen-Exchange Reactions[a]

	//6-31G*		//MP2/6-31G*					
	6-31G*	MP4/ 6-31G*	MP2/ 6-31G*	MP4/ 6-311G**	MP4/ 6-31+G(2d,p)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
N_2 + *cis*-N_2H_2	62.2	27.6	19.5	21.3	23.9	20.7	−36.8	31.7
trans-$N_2H_2 + N_2H_4(C_{2h},TS_2)$	67.2	26.5	17.1	20.8	23.9	20.1	−42.4	32.7
trans-$N_2H_2 + N_2H_4(C_i,SS_2)$			16.8	21.2	23.6	23.3	−38.4	34.7
$C_2H_2 + C_2H_4$	90.1	61.3	54.6	55.6	56.8	53.4	−37.2	64.5
$C_2H_4 + C_2H_6$	80.6	55.6	50.4	49.7	51.5	48.1	−39.1	59.7

[a] Energies in kcal/mol, and $\Delta S^{\ddagger}$ in cal K^{-1} mol^{-1}. $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ at 298 K and 1 atm.

hydrogen-transfer reactions were located and optimized by searching for energy minima under the constraint of having four equal N–H (bridging) bond lengths. These minima were then confirmed as transition structures by verifying that they had only one imaginary vibrational frequency. Table I contains total electronic energies calculated at various levels, and zero-point energies and entropies calculated at the HF/6-31G* and MP2/6-31G* levels. Force constant matrices were obtained by numerical differentiation of the analytical first derivatives. Figure 1 contains selected geometric parameters of species optimized at the MP2/6-31G* level. Computer-generated internal coordinates are available as supplementary material. NBO calculations were performed with the program NBO 3.0.[17] CASSCF calculations were performed with the program GAMESS.[18]

It has been shown[19] that entropies calculated with frequencies at the MP2/6-31G* level are in good agreement with experiment for a variety of small molecules. Values of S° in Table I were obtained from the calculated vibrational frequencies and moments of inertia.

Thermodynamic and activation parameters at 298.15 K and 1 atm are given in Tables II and III for the reactions considered. The highest level calculations were at the full MP4/6-31G* level (i.e., MP4SDTQ) for HF/6-31G* optimized geometries and at the full MP4/6-311G** and MP4/6-31+G(2d,p) levels for MP2/6-31G* optimized geometries. Values of ΔH° were obtained by adding $\Delta(C_v$ integrated from 0 to 298

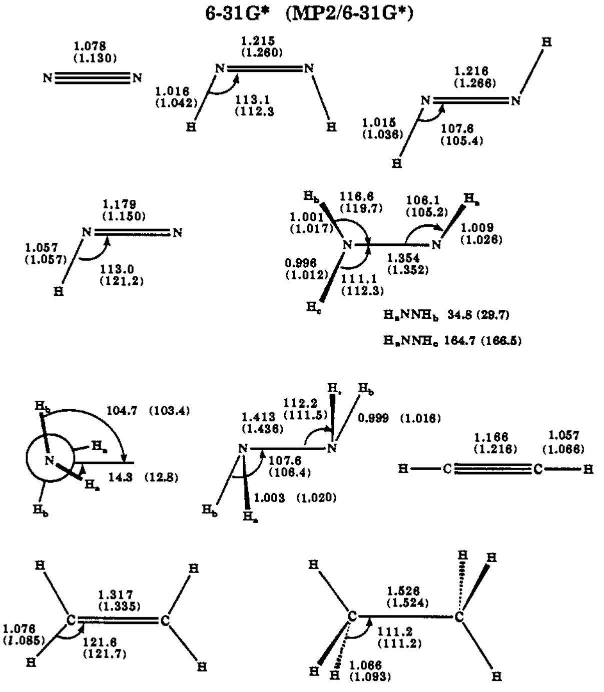

Figure 1. Selected geometric parameters of the reactants and products. The values in parentheses are at the MP2/6-31G* level.

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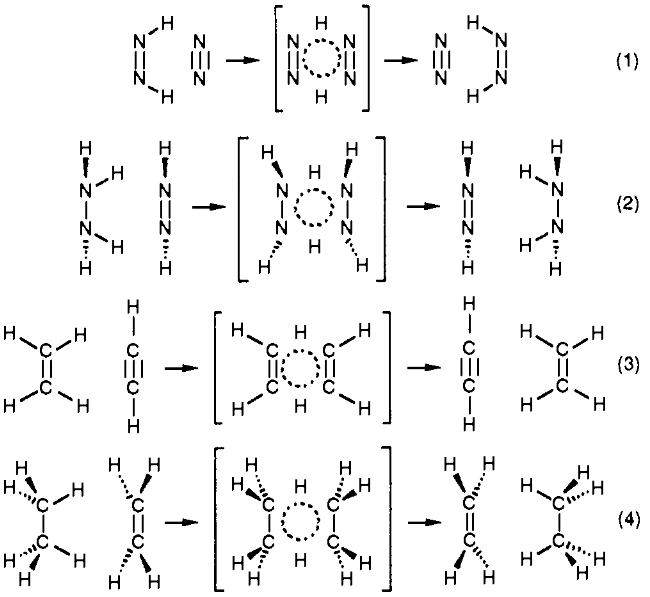
K plus ZPE) at the MP2/6-31G*//MP2/6-31G* level and the electronic energy difference between reactants and products at the MP4/6-31+G-(2d,p)//MP2/6-31G* level. Values of $\Delta H^{\ddagger}$ were obtained likewise, with the additional correction of ΔnRT.

Discussion

Calculations were performed on the transition structures for four concerted pericyclic dihydrogen-transfer reactions:



These four reactions are all degenerate exchange reactions: two of them on nitrogen and two on carbon, two being double/triple bond exchanges, and two being single/double bond exchanges. The primary difference between these and the reactions that we described previously[13] is that the previous reactions are not degenerate and have very large exothermicities.

Quality of Calculations. The primary goal of the calculations was to achieve a degree of accuracy such that differences among the calculated activation energies would be chemically meaningful. As we have discussed previously,[13] an important measure of basis set adequacy is the ability to generate acceptable hydrogenation enthalpies. By this measure, calculations for nitrogen-containing molecules are more demanding than those for hydrocarbons, and acceptable results (±7 kcal/mol) can be obtained at the MP4/6-31+G(2d,p) level. There are no experimental data pertaining to the transition states for these reactions, and so it is more difficult to demonstrate the accuracy of our calculations for these species. In particular, there may be some concern that the transition structures require a multireferential treatment of electronic configuration interaction. We have investigated this possibility by conducting CASSCF calculations on the transition structures located at the MP2/6-31G* level (vide infra). These calculations used the 6-31G* basis set and an active space constructed from all of the excitations from the two highest doubly-occupied orbitals into the three lowest virtual orbitals (four electrons in five orbitals). The coefficients of the SCF configurations in the MCSCF expansion were 0.974, 0.963, 0.979, and 0.971 for reactions 1–4, respectively. These results indicate that the four transition structures are well-represented by the SCF configuration, and therefore perturbative (Møller–Plesset) methods for obtaining electron correlation energies should be adequate.

Stationary States. The calculated energies and entropies of the stationary states are presented in Table I, and the calculated structures of the stable molecules are shown in Figure 1, while Figure 2 shows the geometries of the transition structures.

No comment is required for the stable molecules (with the exception of N_2H_3) because they have been described previously.[13] The structure of N_2H_3 was optimized with unconstrained symmetry. It is in good agreement with that calculated by Pople and Curtiss,[20] and it is qualitatively similar to those obtained at the HF/STO-3G and HF/4-31G levels.[11] If the value of ΔE in Table II for the reaction forming $2N_2H_3$ is combined with ΔZPE from Table I, the NBS value of $\Delta_f H^\circ_0$ for N_2H_4, and the (ΔE + ΔZPE) of hydrogenation of *trans*-N_2H_2 given previously,[13,21] a value of 54.5 kcal/mol is derived for $\Delta_f H^\circ_0$ for N_2H_3; this compares well with the experimental value of 55.3 ± 0.3 kcal/mol recently reported by Ruscic and Berkowitz,[22] but not so well with the value of 62.05 kcal/mol that can be derived from the N_2H_3–H bond energy reported by Grela and Colussi.[23]

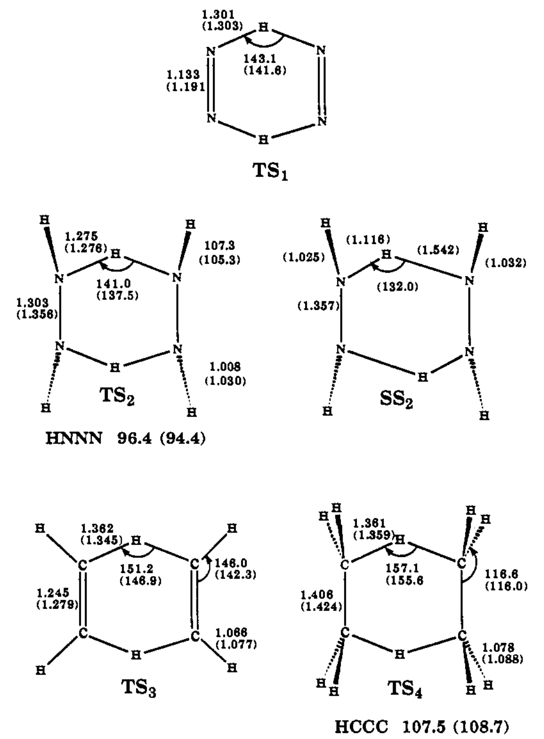


Figure 2. Selected geometric parameters of stationary states other than the reactants and products. The values in parentheses are at the MP2/6-31G* level.

The geometry of the transition structure for the exchange reaction between N_2 and N_2H_2 was optimized at the HF/6-31G* level under D_{2h} symmetry, which led to a single imaginary frequency. The distortion coordinate of the imaginary frequency shows the hydrogen atoms moving as a pair between reactants and products. Thus, the transition structure is exactly concerted; i.e., there is no tendency for the calculated transition structure to distort to the sort of transition structure that would be associated with a stepwise dihydrogen-transfer mechanism. A tight transition structure is indicated by the bond lengths: the N–N bond length is close to the average of the two reactant N–N bond lengths, and the N–H bond length (1.202 Å) is much shorter than the N···H van der Waals contact distance.

Inclusion of electron correlation led only to modest changes in the transition structure geometry. However, as shown in Table III, it led to a huge reduction in the activation energy from 62.2 to 27.6 kcal mol^{-1} at the 6-31G* level. The large reduction of the calculated activation energy was also accompanied by a large decrease in the imaginary frequency from 2737*i* (HF/6-31G*) to 580*i* cm^{-1} (MP2/6-31G*). Such effects are quite common for allowed pericyclic reactions, although the present case may be the most extreme example.[13] Similar electron correlation effects were also found for the other reactions in this study. At the level we believe to be most accurate (MP4/6-31+G(2d,p)//MP2/6-31G*), a value of 20.7 kcal/mol is obtained for $\Delta H^{\ddagger}$ at 25 °C

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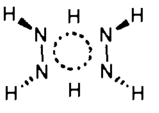
for reaction 1. This value is much less than the enthalpy change associated with the transfer of a single hydrogen atom (73.3 kcal/mol, Table II). It is also much higher than the insignificant activation enthalpies that are calculated for concerted dihydrogen transfer from *cis*-N_2H_2 to *cis*-N_2H_2, *trans*-N_2H_2, and C_2H_4.[13] These latter three reactions are highly exothermic, whereas reaction 1 is strictly thermoneutral. It is reasonable to conclude that the activation enthalpies are related to exothermicities in a direct way as is often found from linear free energy relationships, except the possibility remains that N_2 is somehow anomalous as a dihydrogen acceptor. This possibility is explored in reaction 2. The value of $\Delta S^{\ddagger}$ calculated, −36.8 cal mol^{-1} K^{-1}, is typical for such reactions[13] and contributes significantly to the overall activation free energy.

Reaction 2, in which transfer occurs from hydrazine to diazene, can be discussed in terms of four different transition structures: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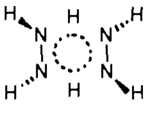
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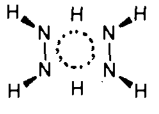
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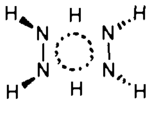
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The first two involve *trans*-N_2H_2, while the second two involve *cis*-N_2H_2. At the HF/6-31G* level, geometry optimization for all four of these structures converged smoothly and gave well-defined transition structures under imposed symmetries of C_{2h}, D_2, C_{2v}, and C_{2h}. They have bridging N–H bond lengths of 1.276, 1.276, 1.263, and 1.269 Å, which clearly identify the species as transition structures for the concerted dihydrogen-transfer reaction. This identification is also supported by the sense of motion in the imaginary modes. Zero-point-corrected activation energies for these transition structures at the MP4/6-31G*//HF/6-31G* level are 25.1, 30.3, 30.5, and 34.7 kcal/mol, respectively.

Isomer **1**, which led to the lowest activation energy, was selected for further study. When this species was subjected to geometry optimization at the MP2/6-31G* level with the same imposed symmetry (C_{2h}), it developed only modest structural differences relative to the HF/6-31G* result, but it was found to have two imaginary frequencies rather than the single imaginary frequency found at the HF/6-31G* level. One of the imaginary modes (a_u, 176*i* cm^{-1}) has the two bridging hydrogen atoms moving according to the reaction coordinate of the concerted dihydrogen-transfer reaction. This is the same normal mode that is imaginary at the HF level. The other imaginary mode (b_g, 335*i* cm^{-1}) has the two bridging hydrogen atoms moving in opposite directions toward the two nitrogen atoms, breaking the C_{2h} symmetry. It is well-recognized that such species (states having two imaginary frequencies) are not transition structures.[24] In an effort to locate the true transition structure at the MP2 level, the imposed symmetry was relaxed to C_i. Under this constraint, a stationary state was located that had a substantially modified geometry, with the bridging hydrogens shifted toward the N_2H_2 moieties so as to generate two equivalent N_2H_3 moieties. A vibrational frequency calculation revealed this structure to be a local energy minimum (two lowest frequencies are a_g = 270 and a_u = 282 cm^{-1}). At this level of calculation it is 0.3 kcal/mol more stable than the C_{2h} double-saddle point and 23.3 kcal/mol more stable than two N_2H_3 radicals (Table II). The existence of such a local minimum would lead to a transition structure of quite low symmetry, as has been found, for example, at certain levels of theory for proton transfer within the formamidine dimer.[25] At the MP4/6-311G** level the situation reverses, with the C_{2h} (concerted) structure being more stable by 0.4 kcal/mol, and at the MP4/6-31+G(2d,p) level the situation reverses yet again, with the C_{2h} structure being less stable by 0.3 kcal/mol. It is clear that the potential energy surface is quite flat near the transition structure for this reaction and that the calculations that would be required to locate the true transition structure on the potential energy surface are currently infeasible. It turns out that the question is not very important in the present case, becaue zero-point and heat-capacity corrections lead to the C_{2h} structure being lower by 3.2 kcal/mol relative to the C_i structure;[26] this difference is largely carried over to differences in free energy. In view of the size of these corrections, the transition state is best modeled by the C_{2h} structure, and our calculated value of 20.1 kcal mol^{-1} for $\Delta H^{\ddagger}$ for reaction 2 (derived from the C_{2h} point) is our best estimate of the true activation enthalpy. This value is still quite substantial when compared to the activation barriers previously reported for the highly exothermic dihydrogen-transfer reactions of *cis*-N_2H_2 with *cis*-N_2H_2, *trans*-N_2H_2, and C_2H_4.[13] These results imply that N_2 is not anomalous as a dihydrogen acceptor, in that the thermoneutral reaction with N_2H_2 as a dihydrogen acceptor (reaction 2) also has a substantial activation enthalpy.

Table IV. Percent Change in Bond Lengths between Reactants and Transition Structure at the MP2/6-31G* Level

reaction	N–H/ C–H, %	acceptor N–N/C–C, %	donor N–N/C–C, %
N_2 + *cis*-N_2H_2	25	5	−5
trans-N_2H_2 + N_2H_4	25	7	−6
C_2H_2 + C_2H_4	24	5	−4
C_2H_4 + C_2H_6	24	7	−6

Geometry optimizations for the transition structures in the reactions of C_2H_4 with C_2H_2 and of C_2H_6 with C_2H_4 (reactions 3 and 4) were conducted with imposed D_{2h} symmetry and led to species with single imaginary frequencies both at the Hartree–Fock and MP2 levels. In both cases the transition structures have geometries obviously corresponding to the concerted dihydrogen-transfer reactions. Moreover, the sense of motion in the imaginary modes is that of both bridging hydrogen atoms moving as a unit from reactants to products. An interesting outcome is that both reactions are calculated to have very large but similar activation enthalpies: i.e., 53.4 kcal mol^{-1} for reaction 3 and 48.1 kcal mol^{-1} for reaction 4.

The trend in our calculated activation enthalpies seems to be that activation energies for thermoneutral dihydrogen transfer do not depend on the bond orders between the heavy atoms, but they do depend on the identity of the heavy atoms. One might hope to rationalize this effect on simple grounds, but as is shown by the data in Table II, it is clear that there is no correlation with bond energies. Perhaps a correlation can be drawn with electronegativities: nitrogen, being more electronegative than carbon, would have more polar transition structures, which could lead to lower activation energies.

Of the four reactions described in this paper, only reaction 4 has been investigated previously.[14] Feller et al. studied reaction 4 by use of the FORS MCSCF method (six electrons in six orbitals). They obtained a transition structure symmetry identical to ours (D_{2h}) and a geometry that was quite similar. However, their zero-point-corrected activation energy is 74 kcal mol^{-1} at 0 K, which is much larger than the result we obtained. The difference arises because the work of Feller et al. does not include treatment of dynamic electron correlation. As noted by Feller et al., the lowest energy configuration had a weight of 92% in the transition structure, which meant that the reaction was symmetry-allowed.[14] This result is in agreement with ours (94% for a four electron in five orbital calculation). Thus, inclusion of a limited number of configurations, as is done in the FORS MCSCF method, does not have much of an effect. The effects of dynamic electron correlation,[27,28] which are well-described by the MP4

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(24) Stanton, R. E.; McIver, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 3632–3646.

(25) Svensson, P.; Bergman, N.-A.; Ahlberg, P. *J. Chem. Soc., Chem. Commun.* **1990**, 82–83.

(26) As a referee has pointed out, the contribution of the b_g mode to the zero-point energy of the C_{2h} structure is not included because the b_g mode is imaginary. If the b_g mode is included in the zero-point energy by treating it as a real frequency (335 cm^{-1}), then the value of $\Delta H^{\ddagger}$ will increase by 0.5 kcal/mol. This change would not alter our conclusion that the C_{2h} structure has an enthalpy lower than that of the C_i structure.

(27) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F. *Theor. Chim. Acta* **1989**, *75*, 81–98.

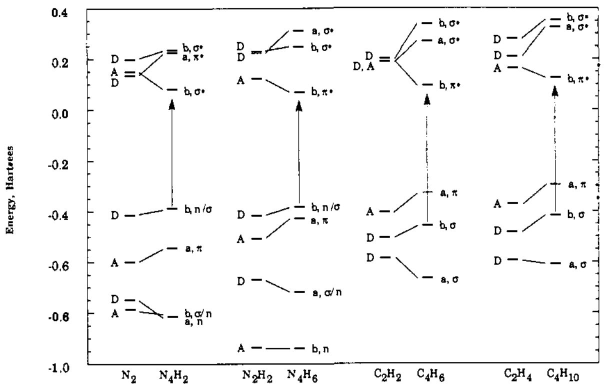

Figure 3. Orbital interaction diagrams computed at the HF/6-311G** level: A = dihydrogen acceptor; D = dihydrogen donor; a = symmetric with respect to the C_2 axis bisecting the two reactants; b = antisymmetric.

method, appear to be much more important.

Analysis of Transition Structures. Reactions 1–4 differ with regard to position in the periodic table and bond orders, but they have formal similarities in that they are all thermally-allowed symmetric dihydrogen-transfer reactions. Moreover, they have substantial similarities with regard to the details of the transition structure geometries. Thus (with the abovenoted caveats regarding the reaction of N_2H_2 with N_2H_4), they all are concerted synchronous reactions having transition structures with C_2 axes, centers of inversion, and σ_h planes relating reactants to products. An even greater degree of similarity is indicated by the percent changes in bond lengths between reactants and transition structures, as shown in Table IV. The fact that these percent changes are almost identical for the four reactions is support for the idea that the transition structures have an equal degree of "tightness".

Despite the similarities noted above, there are large differences among the activation energies for reactions 1–4. In what follows, we consider the origins of these differences by examining (1) orbital interaction diagrams, (2) distortion and interfragment stabilization energies, and (3) NBO (natural bond orbital) analyses.

Examination of Table III reveals that the effects of electron correlation are quite large but uniformly so, so that the trends in activation energy at the MP4/6-31G*//HF/6-31G* level are the same as at the HF/6-31G*//HF/6-31G* level. This observation implies that an understanding of these trends may be obtained by consideration of the molecular orbital interactions. Orbital interaction diagrams for the four reactions are presented in Figure 3. These diagrams are constructed from orbital energies calculated at the HF/6-311G**//MP2/6-31G* level. Reactant orbitals are labeled as A and D, corresponding to dihydrogen acceptor and donor moieties, respectively. They are also labeled a and b, depending on their symmetry with respect to a C_2 axis that bisects the two N–N or C–C bonds. These symmetries constrain the orbital correlations to be drawn between reactants and transition structures.

It is evident that some of the higher-lying bonding MO's rise in energy, while others fall for a given reaction, and there is no strong relationship between the sum of the depicted bonding orbital energy changes and the total energy changes. This lack of correspondence is due, in part, to the behavior of orbitals lying below those included in the diagram. However, an important feature relating to the nature of the bonding *gained* in the transition structure is the charge transfer that arises from an intended correlation between the donor M–H σ (+lone pair) orbital and the acceptor π^* orbital. For the nitrogen-based reactions 1 and 2 this donor orbital is the HOMO, whereas for the carbon-based reactions 3 and 4 the HOMO is a π orbital. Moreover, the energy rise associated with the donor M–H σ (+lone pair) orbital is considerably higher for the carbon-based systems than for the nitrogen-based systems. Thus, the degree of $\sigma \rightarrow \pi^*$ charge transfer is greater for NH than for CH, which leads to a lower activation energy in the NH systems.

Table V. Transition Structure Stabilization Analysis[a]

	N_2 + N_2H_2	N_2H_2 + N_2H_4	C_2H_2 + C_2H_4	C_2H_4 + C_2H_6
ΔE^* MP4/6-31+G(2d,p)	23.9	23.9	56.8	51.5
def energy	43.3	49.2	73.3	66.0
interfrag stabilization	19.4	25.3	16.5	9.2
NBO Energetic Analysis[b]				
acceptor → donor	167.9	188.5	165.2	156.5
donor → acceptor	190.7	213.0	188.6	183.5
(A → D) + (D → A)	275.3	310.7	273.0	260.5
NBO Charge Transfer (e⁻), Donor → Acceptor, 6-311G** Basis				
density: HF	0.26	0.33	0.15	0.18
density: RHO2	0.24	0.32	0.16	0.19
density: MP2	0.24	0.32	0.16	0.20

[a] Energies in kcal/mol. [b] Increase in electronic energy (kcal/mol) due to deleting the indicated group of matrix elements of the Fock matrix. For example, "acceptor → donor" indicates deletion of all Fock matrix elements between occupied orbitals in the acceptor moiety and unoccupied orbitals in the donor moiety. The row "(A → D) + (D → A)" indicates both sets of deletions.

A different perspective on the factors influencing the activation energies can be obtained by a consideration of deformation energies. This concept has been applied previously to transition structures by, for example, Dorigo and Morokuma.[29] Single-point calculations were performed on the donor and acceptor moieties frozen in their transition structure geometries. The deformation energies were then calculated as the difference between the reactants and these transition structure fragments. The differences between these deformation energies and the activation energies are thus the interfragment stabilization energies. These results are presented in Table V. One can view the activation energy as the best compromise between paying the least to deform the reactants and gaining the most from interfragment stabilization. On the basis of deformation energies, the N–H reactions are favored relative to the C–H reactions by about 20 kcal/mol. This effect is easily traced to the greater angular deformations required in the C–H systems. Interfragment stabilization energies also favor the N–H reactions; this is largely due to the $\sigma \rightarrow \pi^*$ interaction discussed above.

NBO analysis provides yet another approach to the problem.[30] When this method is applied to the transition structures discussed in this paper, the molecular orbitals are transformed into NBOs that are largely localized onto one of the classical resonance forms, with the dihydrogen donor on one side and the acceptor on the other. The nature of the charge-transfer interactions can then be probed by performing certain deletions in the Fock matrix and observing the resulting energy changes.[31] For example, diagonalization of the Fock matrix, where matrix elements between high-occupancy NBOs on the dihydrogen donor and low-occupancy NBOs on the acceptor have been deleted, gives a higher energy that indicates the importance of charge transfer from the donor to the acceptor. Such calculations are conducted with the 6-311G** basis set, and the results are presented in Table V. As can be seen, there are large energy effects for charge transfer both to and from the dihydrogen donor, but the predominant effect occurs for charge transfer from the dihydrogen donor to the acceptor. When the concurrent effects of these interactions are

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(28) Simons, J. *J. Phys. Chem.* **1991**, *95*, 1017–1029.

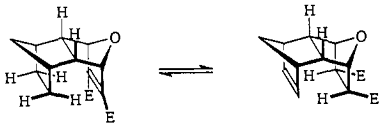
(29) Dorigo, A. E.; Morokuma, K. *J. Am. Chem. Soc.* **1989**, *111*, 6524–6536.

(30) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–928.

(31) The procedure is as described in the NBO 3.0 Program Manual: "This analysis is performed by (1) deleting specified elements (or blocks of elements) from the NBO Fock matrix, (2) diagonalizing this new Fock matrix to obtain a new density matrix, and (3) passing this density matrix to the SCF routines for a single pass through the SCF energy evaluator. The difference between this 'deletion' energy and the original SCF energy provides a useful measure of the energy contribution of the deleted terms."

considered, the same trend is found as in the interfragment stabilization energies. A further application of the NBO method is to calculate the amounts of charge transfer associated with various types of deletions. Charge transfer from the dihydrogen donor to the acceptor was investigated with the 6-311G** basis set with three different density matrices: HF, RHO2 (corrected to second order in Møller–Plesset theory), and MP2 (generalized density corresponding to the second-order energy). Very little difference is seen with the three methods, and all show a significantly larger degree of charge transfer for the nitrogen-based systems than for carbon. Thus, the conclusions derived from the NBO analysis are in agreement with those obtained by inspection of the orbital interaction diagrams and by use of the deformation and interfragment stabilization energies.

Generalities in Dihydrogen Transfer. A wide variety of dihydrogen-transfer reactions may be envisioned. These include the reactions described in this paper, the reaction between CO and hydroxymethylene, the reactions between aldehydes and alcohols, and reactions based on the NO and CN centers. However, very few experimental data concerning the barriers to thermoneutral concerted dihydrogen transfer have been published. Hagenbuch et al. reported on the intramolecular alkene/alkane dihydrogen-transfer reaction



(5)

which has $\Delta H^{\ddagger} = 35\text{–}39$ kcal mol^{-1},[5] and Paquette et al. reported on a similar reaction that has $\Delta H^{\ddagger} = 27$ kcal mol^{-1}.[6] Both of these reactions are nearly thermoneutral. The paper of Paquette et al. also showed that the rate constants for dihydrogen transfer were highly sensitive to the distance between the donor and acceptor sites. In a very recent paper, Paquette et al. show that strain energy is also a significant factor.[32] We inferred from the experimental data that the molecules investigated were constructed in such a way as to reduce the barrier relative to the intrinsic barrier of 48 kcal mol^{-1} that we have calculated. Apparently this was achieved by using the molecular skeleton to force the donor and acceptor sites into close proximity.

There is one other published computational study of degenerate dihydrogen exchange, and it describes the reaction of formaldehyde and methanol.[33] A value of 30.3 kcal mol^{-1} was obtained at the MP2/6-31G*//HF/6-31G* level. This result is intermediate between those obtained in the present study and is consistent with the notion that the activation energies decrease with increasing electronegativity of the heavy atoms.

Conclusions

The symmetric dihydrogen-transfer reactions between N_2H_2 and N_2, C_2H_4 and C_2H_2, and C_2H_6 and C_2H_4 have pericyclic transition structures with synchronous motion of the transferring hydrogen atoms. This also appeared to be the case in the reaction of N_2H_4 with N_2H_2, although we were not able to locate the exact transition structure. Electron correlation is very important in determining the activation energies, and when it is included results are obtained that are reasonably consistent with the experimental results for intramolecular transfer between aliphatic and olefinic moieties. The computed activated energies are highly sensitive to the atomic number of the heavy atoms in the cyclic transition structure, but not to bond order. Major factors controlling the activation energies appear to be (1) the amount of deformation energy expended to attain the cyclic transition structure and (2) the transition structure stabilization gained by charge transfer from the dihydrogen donor to the acceptor. We propose that, with proper modification of the reactants (achieved, perhaps, by introducing electron-withdrawing substituents into the hydrazine–diazene reaction), thermoneutral dihydrogen transfer could be a rather facile process.

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Registry No. (*Z*)-Diazene, 15626-42-3; nitrogen, 7727-37-9; hydrazine, 302-01-2; (*E*)-diazene, 15626-43-4; ethene, 74-85-1; acetylene, 74-86-2; ethane, 74-84-0; diazenyl, 36882-13-0; hydrogen, 1333-74-0.

Supplementary Material Available: Computer-generated coordinates (*Z*-matrix) for the dihydrogen-transfer reactions (7 pages). Ordering information is given on any current masthead page.

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