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Dissociation of diimide

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Parts of the potential energy surface of N_2H_2 have been studied using CASSCF- and contracted CI-methods. Of particular interest was the concerted dissociation of *cis*- and *trans*-diimide into N_2 and H_2, since the *trans*-dissociation is symmetry allowed and the *cis*-dissociation forbidden. Three different saddle points were located, of which only one, of C_{2v}-symmetry, is a true transition state. Elaborate numerical gradient methods using exact Hessians and update procedures had to be used to find these saddle points on the unexpectedly complex N_2H_2-surface. The barrier height with respect to *trans*-diimide is 61 kcal/mol after vibration correction. Since this energy is higher than the barrier for interconversion, *cis*- and *trans*-diimide have the same transition state. It is further found that diimide preferably dissociates stepwise, by losing one hydrogen at a time, rather than in a concerted way. This conclusion is drawn basically because the geometry of the transition state for the concerted dissociation has a very long H-H distance of 5.6 a.u. The N-H bond energy in trans-diimide is 56 kcal/mol after vibration correction.

Key words: Diimide—dissociation of ~

1. Introduction

Molecular orbital symmetry arguments have been of great importance in understanding the mechanisms of organic reactions [1, 2]. Based on the success of the simple symmetry rules in this area, these rules are now being widely used also for inorganic and metallo-organic reactions [3, 4]. There are however many reasons to suspect that the situation is not quite as simple in these reactions as it is for the usual organic reaction. In a typical organic reaction stable closed shell reactants are converted into stable closed shell products. Complicating near degeneracy effects are usually not present. Mechanisms for reactions where radicals are involved are often even simpler to predict. In metallo-organic chemistry the opposite is generally true. It is very unusual that reactants and products are stable closed shell molecules and near degeneracy effects are practically always present. The large correlation effects in the *d*-shell is another complicating factor. In inorganic chemistry even simple stable molecules like NO and O_2 are not of closed shell type. Nor do they in any way resemble radicals in the organic chemical sense. The near degeneracy effects are not only a problem for a simple qualitative understanding, they have also so far in large prevented the application of rigorous *ab initio* methods on these problems. To treat a metallo-organic reaction, the methods must be able to include the important dynamical correlation effects in the presence of bond-breaking and bond formation processes, which quickly requires very long CI-expansions. For inorganic chemical reactions the situation is often very similar, particularly for electron rich molecules. During recent years great progress has been made in the development of MCSCF- and CI-methods capable of treating these complicated reactions, and simple model reactions can now begin to be accurately handled. A series of calculations on such reactions has therefore recently been performed and will be presented in separate papers. As models for metallo-organic reactions, the reductive elimination of H_2 from NiH_2 [5] and C_2H_6 from $Ni(CH_3)_2$ [6] have been studied. In order to find out if NO_3 is an intermediate in the thermolecular formation of NO_2 from NO and O_2, calculations were performed for the dissociation of NO_3 [7]. Both NiH_2 and NO_3 are examples of cases where qualitative symmetry arguments have been used earlier to analyze the reaction mechanisms [4, 8]. From the large CI-calculations a different and new reaction mechanism was suggested for the forbidden reactions, by which a simple symmetry rule could be formulated. This rule says that forbidden reactions which can proceed stepwise, having the occupation in each symmetry changed by only one unit in each step, have lower barriers than when this is not possible. This means for example that the $^2A_1$-state in NO_3 has a lower barrier for dissociation than the $^2A_2$-state, and that the $^3B_1$-state in NiH_2 has a lower barrier than the $^3A_1$-state. It should be emphasized in this context that the complexity of the large CI-calculations does not rule out simple qualitative pictures of the reaction mechanisms. In another study the barrier for dissociation of SiH_5^- was calculated [9] to test previously given qualitative symmetry arguments given for the isoelectronic PH_5 [10]. The CI-calculations on SiH_5^- gave a very complicated dissociation mechanism however, indicating that the symmetry rules are not so useful in this case.

In the present paper a study of the seemingly simple dissociation reaction $N_2H_2 \rightarrow N_2 + H_2$ will be presented. Since the *trans*-diimide reaction is allowed, and the *cis*-diimide reaction is not allowed by orbital symmetry rules, see Fig. 1, one question of interest is to see how this difference affects the respective barrier heights for dissociation. It is clear that one should not expect that the *trans*-reaction will proceed without a barrier and the *cis*-reaction with a very high barrier, but one ought to find a clear difference if symmetry rules should be considered useful in this case. The second chemical problem which was studied was the question whether diimide dissociates in a concerted manner or if the

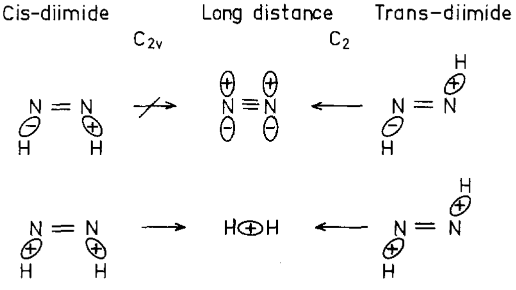

Fig. 1. Molecular orbital correlations for the *cis*-diimide (C_{2v}) and the *trans*-diimide (C_2) dissociations

process is stepwise by the loss of one hydrogen at a time. The experimental evidence favours the stepwise dissociation [11]. In the calculations it is natural to apply a symmetry constraint on the concerted reactions. The *cis*-dissociation was therefore studied in C_{2v}-symmetry and the *trans*-dissociation in C_2-symmetry. The obtained saddle points then have to be checked by releasing the symmetry constraints to see if they represent true transtion states having only one negative eigenvalue of the Hessian matrix. The potential surface for N_2H_2 turned out to be extremely complex. A true transition state for the *trans*-dissociation was finally found with a barrier height of 66 kcal/mol after vibration corrections. This transition state is rather surprisingly of C_{2v}-symmetry. For the C_{2v}-constrained *cis*-dissociation another saddle point with a shorter H-H distance was found. This saddle point is, however, not a true transition state, and has an energy which is much higher than the *trans*-dissociation saddle point. Since the true transition state is higher in energy than the barrier for interconversion between *cis*- and *trans*-diimide [12], it is clear that the two isomers have the same transition state for concerted dissociation. Probably *cis*-diimide will have to go through a non-C_{2v} reaction path to reach this transition state. For the stepwise dissociation, the removal of the first hydrogen, which proceeds without a barrier, requires an energy of 61 kcal/mol for *trans*-diimide. Removal of the second hydrogen goes over a barrier which is substantially lower than the energy required to take the first hydrogen away. The concerted and stepwise dissociation consequently have rather similar barriers. The present calculations are not accurate enough to produce numbers which conclusively say which of these mechanisms is preferred. The best argument for a stepwise dissociation is however found from the geometry of the transition state for the concerted dissociation. The H-H-distance is very long which makes it unlikely that this is the most favourable pathway. The energy barrier is further very close to the sum of the energies required to break both bonds, which indicate very little interaction between the hydrogens. This is discussed further in Sect. 3. The stepwise dissociation should therefore be preferred, which is in agreement with most experimental evidence. In summary, the orbital symmetry rules were consequently not found to be too useful for the N_2H_2 dissociation.

Besides the more chemical problems, which were attacked by the present calculations, there was also a purely technical one, namely the problem of locating the saddle points. This problem turned out to be much more difficult than anticipated based on earlier experience. For example, locating the saddle point for the dissociation of NO_3 into NO and O_2 [7], for the linear dissociation of C_2H_2 into 2CH [13] or for the dissociation of CH_4^{2+} into $CH_3^+ + H^+$ [14] was very much easier. There are two complicating factors for the N_2H_2 dissociation which were not present in these other cases. First, there are at least three strongly coupled degrees of freedom for any reasonable choice of internal coordinates. This means that any method based on initial one- or two-dimensional search directions will fail. Rather surprisingly the nitrogen-nitrogen distance has a very strong influence on the location of the saddle point. This makes the diimide dissociation quite different from for example the formaldehyde dissociation. The second complicating factor, which probably is connected with the first one, is that there are other saddle points, with more than one negative eigenvalue of the Hessian, in the same area as the correct saddle point. Two sophisticated, and rather expensive, techniques were finally combined to successfully locate the saddle points. In the first one the area of the saddle point was located by searching on successively smaller hyperspheres [15]. When the transition state area was reached an exact Hessian was calculated followed by a minimization of the gradient, including a Hessian update procedure [16]. It is believed, however not proved, that both the use of the exact Hessian and the update procedure were necessary for finding the saddle point for the *trans*-dissociation. What has been shown is that some common techniques, which usually work well, particularly for locating local minima, do not work in this case. These methods include for example polynomial fits to calculated points followed by the Newton–Raphson procedure, and also the start with a reasonable diagonal Hessian followed by update procedures. Two points should be stressed in this context. First, some of these mentioned techniques will of course succeed in finding the saddle point if the starting point is very close to the saddle point. Second, even the combined methods from Refs. [15, 16] initially converged to the wrong saddle point. The details of the location of the saddle points are described in Sect. 4.

Electronic structure considerations, including the nature of the different saddle points, are described in Sect. 3. Of particular interest are the different saddle points found for the diimide dissociation. The true transition state, which has only one negative eigenvalue of the Hessian, probably corresponds to dissociation into $N_2 + H_2$. One other saddle point, with two negative eigenvalues of the Hessian, leads to dissociation into three products, $N_2 + H + H$. In a recent paper Osamura et al. [17] found a similar stationary point for glyoxal dissociation, and concluded that this reaction "would be unique among energetically understood processes in that it is a unimolecular reaction involving one transition state and three molecular products". It may appear that dissociation of *trans*-diimide could also be such a case. This is however not concluded here. Some of the differences between the diimide and the glyoxal dissociation will be discussed in Sect. 3.

3. Computational details

CASSCF [18] and contracted CI [19] calculations have been performed for *cis*- and *trans*-N_2H_2, for $N_2H + H$, for $N_2 + H_2$ and for the transition states for dissociation of N_2H_2. Two different basis sets have been used, of double zeta and triple zeta+polarization quality. The details of these calculations are described in this section.

Most of the calculations reported here were done with the Huzinaga-Dunning [20, 21] $9s, 5p$-set contracted to $4s, 2p$ for nitrogen and $4s$ contracted to $2s$ for hydrogen. All geometry optimizations for the different local minima and for the saddle points were done with this basis set. For selected points a larger basis set was used with $10s, 6p$ contracted to $5s, 4p$ for nitrogen and $5s$ contracted to $3s$ for hydrogen [20, 22]. Polarization functions were added for this basis set with d-exponent 0.95 and p-exponent 0.65. The local minima were re-optimized with this larger TZ+P basis set, but not the saddle points however, since this was considered to be too expensive and would probably not change any of the conclusions made. For the geometry optimizations a C_2-symmetry constraint was used for *trans*-N_2H_2 and its dissociation, and a C_{2v}-symmetry constraint for the corresponding *cis*-dissociation. For the saddle points additional non-symmetrical calculations were performed to check the number of negative eigenvalues of the Hessian.

All geometry optimizations were done at the CASSCF-level. The orbital optimization was done using the Newton-Raphson procedure with the exact orbital Hessian. No orbital-CI coupling was included, but convergence to six decimal places in the energy was anyway reached in only 4-5 iterations with starting vectors from a nearby point. The nitrogen $2p$-orbitals and the hydrogen $1s$-orbitals were active, which means full distribution of 8 electrons in 8 orbitals. The nitrogen $1s$- and $2s$-orbitals were inactive. This means 900 configurations for the C_2-constrained *trans*-geometries and 480 configurations for the C_{2v}-cinstrained *cis*-geometries. N_2H was described by 404 configurations and N_2 by 32 configurations. Based on experience from N_2 [19] and C_2H_2 [13] this configuration space should give accurate potential surfaces. For both N_2 and C_2H_2 large multi-reference CI-calculations gave quantitatively very similar results to what was found at the CASSCF level. It is therefore likely that the basis set limitations are the most severe restrictions in the present calculations. As will be seen in Sect. 3 below, the difference between the DZ and TZ+P results for the barrier heights, for example, was however surprisingly small. This should be an indication that even larger basis sets should not qualitatively change the picture of the reactions given here.

A few contracted CI calculations were performed at the most important geometries using the TZ+P basis set. Configurations with coefficients larger than 0.05 in the preceding CASSCF calculations were selected as reference states for the single and double excitation CI. This procedure means that different configuration spaces were selected for the different geometries. Earlier experience [19] suggest that balanced energy differences between different areas of a potential surface will any way be obtained, basically because such a large fraction of the correlation energy is calculated. For *cis*-diimide 5 reference states yielding 123 711 configurations were selected. The corresponding numbers for the C_{2v} saddle points were 8 and 152 505, for *trans*-diimide 4 and 95 509 and for N_2H 5 and 173 637. The multi-reference analogue of Davidson's correction [23] was finally calculated in each point. The timings for the largest contracted CI calculations were 2-3 hours on the VAX-11/780.

3. The dissociation reactions of diimide

The different mechanisms for dissociation of diimide will be discussed in this section. Three different saddle points for concerted dissociation were found and the nature of these stationary points is analyzed. The electronic structure of the different isomers appearing on the N_2H_2 potential energy surface is also described.

The thermochemistry of the isomers of N_2H_2 has been the subject of intense theoretical and experimental interest (see Ref. [24] for further references), particularly because diimide is widely used as a reagent in the stereospecific hydrogenation of double bonds. The mechanism for hydrogenation requires an isomerization from the more stable *trans*-diimide to *cis*-diimide, which is believed to be the rate-determining step. Since the experimental activation energy is only around 4 kcal/mol and theoretical inversion and rotation barriers are around 50 kcal/mol other possible pathways have been suggested. This particular problem will not be discussed further here, but various results from these investigations will be useful in the present context, both for providing additional information of the N_2H_2 potential energy surface and also for comparisons with the present calculations.

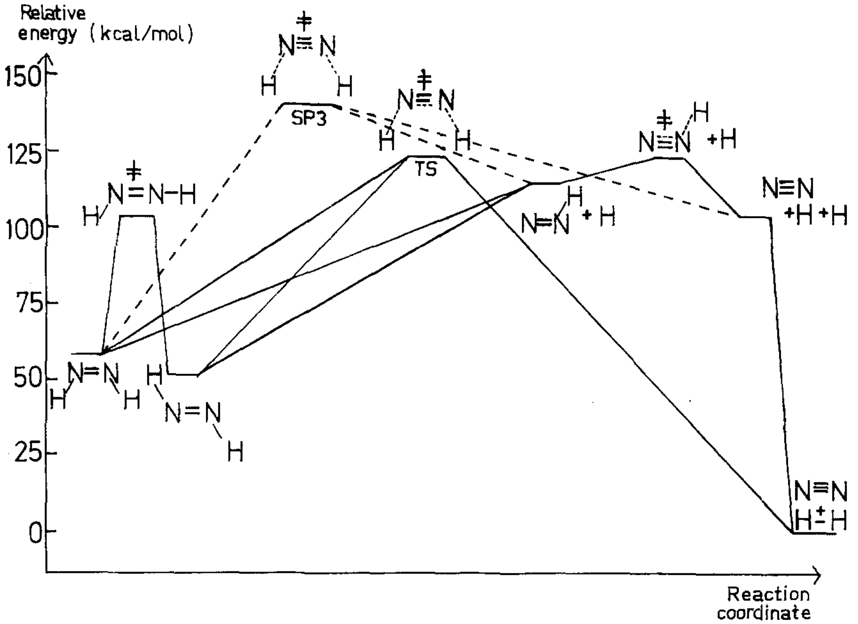

Fig. 2. Relative energy at the CI + Davidson's correction level for different points on the N_2H_2 potential energy surface

Fig. 2 pictures schematically the relative energies for different points on the N_2H_2 potential energy surface and the reaction pathway between these points. The detailed energies from the present calculations are also summarized in Table 1. In Fig. 1 the energies are mostly taken from the CI-level including Davidson's correction. When the results at the CI-level are discussed below, Davidson's correction is always included. The optimized geometries for the DZ basis set at the CASSCF-level are given in Fig. 3 and the TZ + P geometries in Table 2, where they are compared with earlier calculations and experiments. *Trans*-diimide is the only one of the isomers treated here, where the geometry is known experimentally. This geometry is very accurately reproduced by the TZ + P-calculations, which is also valid for the SCEP-optimized geometry in Ref. [25], where a similar sized basis was used. The geometry optimized in Ref. [12] is only at the SCF-level and the bonds, particularly the N–N bond, are therefore too short. The bond-distances change only slightly from *cis*- and *trans*-diimide and the angle agrees again well with what was found in Ref. [25]. For the experimentally unknown

Table 1. Relative energies between different points on the N_2H_2 potential energy surface (kcal/mol)

	CASSCF DZ	CASSCF TZ+P	CI TZ+P	CI+Dav. corr.
N_2+H_2	0	0	0	0
		0	0	0
		0	0	0
N_2H_2-*trans*	53.4	59.9	58.4	51.1
		67.4	65.9	58.6
		67.7	67.9	59.1
N_2H_2-*cis*	63.8	67.0	66.1	58.5
		74.0	73.1	65.5
		74.1	69.0	61.5
N_2H+H	116.3	129.6	124.3	116.8
		128.6	123.3	115.8
		124.4	122.7	115.5
N_2+H+H	91.1	94.8	105.5	105.5
		88.5	99.2	99.2
		88.5	99.5	99.5
Transition state[a]	120.4	128.2	134.2	124.5
		123.6	129.6	119.9
Saddle point 2[a]	151.7	156.7	158.0	150.7
Saddle point 3[a]	142.1	—	—	—

The first entry at the DZ-optimized geometries,
the second entry at DZ-optimized geometries + vibr. correct. and,
the third entry at TZ + P-optimized geometries + vibr. correct.

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[a] See Fig. 2

Table 2. Optimized geometries and energies (a.u.) for *trans*- and *cis*-diimide and the diazenyl radical

	Present results[a]	Casewit, Goddard [24][b]	Ahlrichs, Staemmler [12][c]	Parsons, Dykstra [25][d]	Exp. [29]
N_2H_2-*trans*					
r_{NN}	2.38		2.28	2.35	2.366
r_{NH}	1.97		1.93	1.94	1.943
θ_{NNH}	106.4°		109°	106.1°	106.8°
E	−110.4100		−110.3755	−110.3706	
N_2H_2-*cis*					
r_{NN}	2.37		2.28	2.36	
r_{NH}	1.98		1.95	1.96	
θ_{NNH}	111.1°		114°	112.3°	
E	−110.4054		−110.3665	−110.3331	
N_2H					
r_{NN}	2.24	2.28			
r_{NH}	2.04	1.99			
θ_{NNH}	113.2°	114.6°			
E	−109.8068	−109.5832			

[a] TZ+P, CASSCF-level geometry optimization. Energy for CI+Dav. corr.
[b] DZ+P, GVB-CI-level geometry optimization and energy.
[c] DZ+P, SCF-level geometry optimization. CEPA-energies.
[d] TZ+P, SCEP-level geometry optimization and energies

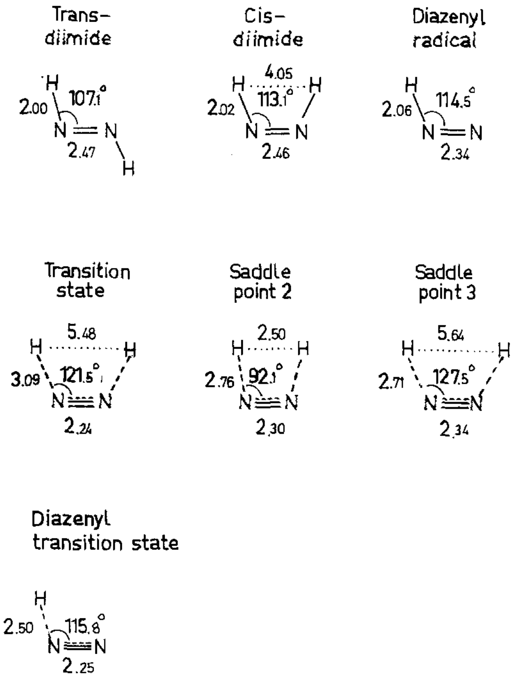

Fig. 3. Geometries obtained at the CASSCF level, using ghe DZ basis set

diazenyl radical the predicted geometry differs slightly from the GVB-CI optimization in Ref. [24]. The N-N-bond is shorter by 0.04 a.u. and the N-H-bond is longer by as much as 0.05 a.u.. The DZ-optimized geometries in Fig. 3 have as expected longer bonds than the TZ+P-geometries in Table 2. Particularly the N-N-bond is sensitive to the basis set and comes out around 0.1 a.u. longer at the DZ-level.

The by far lowest energy on the potential surface is obtained for N_2+H_2, which is 59 kcal/mol more stable than *trans*-diimide at the CI-level with the TZ+P basis set. At the CASSCF-level this energy goes from 53 kcal/mol with the DZ basis to 60 kcal/mol using the TZ+P basis. The correlation effect is only 2 kcal/mol. Diimide is consequently only at a local minimum, but has a very long life time because of the high dissociation barriers. In agreement with most earlier calculations and experiments *trans*-diimide is found to be slightly more stable than *cis*-diimide. The energy difference between *cis*- and *trans*-diimide varies a few kcal/mol between different levels of theory. The value at the CI-level with geometries optimized at the CASSCF-level with the TZ+P basis set is 2 kcal/mol, which can be compared to the most accurate results from the literature of 5 kcal/mol [24] and 6 kcal/mol [12]. For the DZ-optimized geometries the CI-value increased to 7 kcal/mol, which gives an indication of the size of the errors introduced by using slightly non-optimal geometries. The electronic structure of *cis*- and *trans*-diimide is very similar. The leading Hartree-Fock configuration has a coefficient of 0.95 at the CASSCF-level for both isomers, with only one other important configuration $\pi^2 \rightarrow (\pi^*)^2$ having a coefficient of 0.20. The dipole moment is 3.1 D for *cis*-diimide at the CI-level. Interconversion between *trans*- and *cis*-diimide goes preferably through inversion rather than rotation, with the most accurate literature value 55 kcal/mol [12].

The first saddle point located on the N_2H_2 surface was for the concerted dissociation of *cis*-diimide. A C_{2v}-symmetry constraint was used, resulting in the geometry given in Fig. 3 for saddle point 2. The N_2-H_2 distance is 0.9 a.u. larger than in *cis*-diimide, and both the H-H- and the N-N-distances have changed to values halfway between the *cis*-diimide values and the asymptotic values. These changes correspond well to the change in electronic structure. From Fig. 1 it is seen that the major change in the *cis*-dissociation is changing a doubly occupied b_2-orbital to a doubly occupied a_1-orbital. At the saddle point the occupation number of the b_2-orbital is 1.2 and the a_1-orbital 0.8. The *cis*-diimide configuration has a coefficient of 0.72 and the product configuration 0.59. The dipole-moment has further decreased drastically to 0.8 D. The energy difference relative to *cis*-diimide is not as high as 92 kcal/mol at the TZ+P, CI-level. Since it was considered to be too expensive to reoptimize the geometry for the saddle point for the larger basis set, the energy comparisons are made consistently at DZ-optimized geometries. As mentioned above this geometry error gave a relative energy error of only 3 kcal/mol between *cis*- and *trans*-diimide. It is however reasonable to expect a slightly larger error for the barrier height, since the saddle point energy is more sensitive to geometry changes. We note though, that the barrier heights obtained at the three different levels of theory are very similar 88, 90 and 92 kcal/mol. So far the results are consistent with the orbital symmetry rules, which does predict a high barrier for the non-allowed *cis*-dissociation. We note in this context that the barrier height of 92 kcal/mol is much higher than the barrier height of 56 kcal/mol for inter-conversion to *trans*-diimide. If there would exist a lower barrier for *trans*-dissociation, which is predicted by orbital symmetry, the C_{2v}-constrained saddle point for *cis*-dissociation would therefore be of only academic interest.

To finally check if saddle point 2 is a true transition state, second derivatives of the energy were calculated with respect to distortions away from C_{2v}-symmetry. In C_{2v}, the Hessian matrix has only one negative eigenvalue, corresponding to the concerted dissociation. Using the orbital symmetry rules it is expected that an a_2-distortion to C_2-symmetry would give another negative eigenvalue since the C_2-pathway is symmetry allowed and the C_{2v}-pathway is not. The a_2-distortion had a minimum in C_{2v}, however. On the other hand the b_2-distortion, where one N-H-distance is lengthened, gave an energy maximum. Saddle point 2 is therefore not a true transition state, which is not so surprising with such a high energy. Removing both hydrogens simultaneously out to N_2 and two separated hydrogens should require less energy, not to mention a step wise dissociation.

The saddle point for *trans* dissociation, with a C_2-symmetry constraint, turned out to be much more difficult to locate than for the *cis*-dissociation. The details of the location of the saddle points are described in the next section. The first saddle point which was found, saddle point 3 in Fig. 3, had two negative eigenvalues of the Hessian in C_2 and could consequently not correspond to a true transition state. The direction of one of the eigenvectors with negative eigenvalue leads for this saddle point to dissociation into three products, $N_2 + H + H$. The dissociation into three products seems also likely with an H-H-distance of 5.6 a.u. as compared to the C_{2v} saddle point 2 which had an H-H-distance of only 2.5 a.u.. The electronic structures of these two saddle points are otherwise very similar, the only real difference being that the leading configurations for the C_2 saddle point have coefficients 0.65 and −0.65 compared to 0.72 and −0.59 for the C_{2v} saddle point.

The barrier height for the C_2 saddle point is 88 kcal/mol with respect to *trans*-diimide at the DZ-basis, CASSCF-level, which is slightly lower than the C_{2v}-constrained saddle point for the *cis*-dissociation. No calculations with the larger basis set at the CI-level were done for saddle point 3. A search for a saddle point of lower energy and of a true transition state nature was made instead.

After a considerable effort, see Sect. 4, a second saddle point was finally found, which rather surprisingly is of C_{2v}-symmetry like saddle point 2. This saddle point has only one negative eigenvalue of the Hessian in C_2. The barrier height with respect to *trans* diimide is 73 kcal/mol at the TZ+P, CI-level. After vibrational correction the barrier drops to 61 kcal/mol. As for the other saddle points, a b_2-distortion of the N-H bond lengths was made to determine the sign of the second derivative. Also, for the sake of completeness, a check was made for the missing sixth degree of freedom, the b_2 antisymmetric combination of the NNHbendings. The new saddle point was found to be at a minimum in both cases and is consequently a true transition state. Since the barrier height is considerably lower than what was found for saddle point 2, this new point apparently serves as transition state for the *cis*- as well as for the *trans*-dissociation. The reaction path for the *cis*-dissociation probably has to go through nonC_{2v}-symmetries, most likely with b_2-distortions, to avoid the saddle point 2. The geometry for the transition state is shown in Fig. 3. In spite of the long H–H-distance, dissociation along the direction of the eigenvector with the negative eigenvalue seems to lead to $N_2 + H_2$, but $N_2 + H + H$ are also possible products. The barrier height is anyway close to the sum of the energies required for removal of the first hydrogen from N_2H_2 and the second hydrogen from N_2H (see below). The main difference in geometry between the transition state and saddle point 2 is the H–H-distance. The N–N-distance is also slightly closer to the triply bonded N_2 for the transition state, whereas the N_2H_2-distance is very similar in the two cases. The H–H-distances are on the other hand similar for the transition state and saddle point 3. These features are characteristic for the whole N_2–H_2-surface. There are for each N_2–H_2-distance two minima for the H–H-distance, one for a long distance corresponding to the diimide H–H-distance, the other for a short distance corresponding to the H_2-molecule. In the region between these minima the potential surface is very flat. The H–H- and the N–N-distances are further strongly coupled, which leads to the severe problems in locating the saddle point. The electronic structure of the transition state is finally rather similar to that of saddle point 3, with CI-coefficients of 0.82 and −0.47 for the leading configurations. The dipole moment is 0.5 D.

With these results in mind one could start to evaluate the predictions made by the orbital symmetry rules. On the most important point these rules are not too useful in this case. The barrier for *trans*-dissociation is not lower than for *cis*-dissociation. In fact, since they have the same saddle point, and *trans*-diimide is lower in energy than *cis*-diimide, the barrier for *trans*-dissociation is really higher. Orbital symmetry also says that there should probably be a lower barrier in C_2-symmetry than in C_{2v}-symmetry, which was also contrary to what was found. The reason for the small use of the orbital symmetry rules for the diimide dissociation is of course the small overlap between the hydrogens. The point where the overlap is large enough to make the orbital symmetry rules useful is not obvious, and must be a matter of experience. It is expected that calculations of this type should be helpful in this respect.

The second question, which the present calculations should answer, is whether the dissociation of N_2H_2 is concerted or stepwise. For this reason a single hydrogen was gradually pulled off at the DZ, CASSCF-level of theory. The energy increased smoothly all the way to the dissociated products and no barrier was found. Optimization of N_2H at the TZ+P, CASSCF level followed by contracted CI-calculations + Davidson's correction, led to a bond energy of 65 kcal/mol, calculated as the difference between *trans*-N_2H_2 and $N_2H + H$.

After vibrational correction the bond energy is reduced to 56 kcal/mol, which should be compared to the barrier height for the concerted dissociation which was 61 kcal/mol. We belive that this energy difference is conclusive, but a different result using a larger basis set and a better geometry optimization can not safely be ruled out. A disturbing fact is the large difference in the bond energy of N_2H_2 obtained here and in Ref. [24], where a vibration corrected value of 70.0 kcal/mol was reported. A closer analysis shows that out of the total 14 kcal/mol energy difference between the results, 8 kcal/mol come from the different unlinked cluster corrections used here and in Ref. [24]. Davidson's correction was used here and "retention of bondedness" in Ref. [24]. Which one of these correctios is the most reliable in the present case is difficult to predict and only future, more accurate calculations can decide this question. Returning to the question whether dissociation of diimide is stepwise or concerted, another more qualitative argument can also be used. With the very large H-H bond distance obtained for the transition state, it is hard to believe that the hydrogens overlap sufficiently to "help each other" over the barrier. It is much more likely that the hydrogens in fact move independently from each other, and in this case a stepwise dissociation must always be preferable. If there is no interaction between the hydrogens the barrier height in the concerted case will be equal to the sum of the energies required to remove the hydrogens separately. This is in fact very close to what is found from the calculations. The difference is less than 1 kcal/mol. In the stepwise dissociation it will be equal to the maximum energy required to remove only one, which must of course always be smaller in this extreme.

In a recent article Osamura et al. [17] studied the concerted dissociation of glyoxal, $H_2C_2O_2$, into the three products $H_2+CO+CO$. It is interesting to draw some parallells between the glyoxal and the diimide potential surfaces. In both cases saddle points exist which give dissociation into three products. Whereas this was shown to be the most favourable pathway to three separated products for glyoxal, this is not so for diimide. The difference is seen very clearly on the molecule left, when one of the three products is split off. In glyoxal, when one CO is taken away, the remaining atoms in H_2 and CO rearranges to form the very stable bonds of formaldehyde, H_2CO. When one hydrogen is taken off diimide, on the other hand, the remaining atoms stay basically in their original positions and form the very unstable molecule N_2H. In glyoxal it is therefore an advantage, if three products should be formed, not to allow the H_2 and CO rearrangement to formaldehyde to take place, but rather remove the second CO at once, which leads to the low lying transition state for dissociation into three products. No such advantage is present for diimide.

4. The location of the transition states

The transition states for the dissociation of *trans*- and *cis*-diimide into N_2 and H_2 were difficult to locate. In this section some of the experience from this work will be summarized.

Given two points on a potential energy surface, corresponding to the reactants and products in a chemical reaction, one usually defines the transition state (TS) for the reaction as the highest stationary point on a continuous minimum energy path linking both ends of the reaction. From this definition the potential energy function $E(\boldsymbol{q})$, $\boldsymbol{q} = (q_1, q_2, \ldots, q_{3N-6})$, has to satisfy the following two conditions at the TS:

i) The energy gradient must vanish.

$$g(\boldsymbol{q}) = \boldsymbol{0} \tag{1}$$

where

$$g_i(\boldsymbol{q}) = \partial E(\boldsymbol{q})/\partial q_i, \qquad i = 1, 2, \ldots, 3N\text{-}6 \tag{2}$$

ii) The Hessian matrix $\boldsymbol{A}$

$$[A(\boldsymbol{q})]_{ij} = \partial^2 E(\boldsymbol{q})/\partial q_i \, \partial q_j \tag{3}$$

must have one and only one negative eigenvalue.

i) and ii) are usually taken to be sufficient conditions on the TS of a concerted reaction. In spite of these clearly formulated criteria, the difficulties encountered when searching for transition states are often considerable. The energy function is in most quantum chemical procedures not analytically available, but has to be defined numerically point by point. A natural and well established approach is to try to satisfy i) by minimizing the gradient norm [26]. This method is particularly useful when the energy gradient is analytically available in each point, but can also be applied by using numerical first derivatives. In the present calculations analytic gradients were not at hand, since there has not yet been implemented a gradient facility in the CASSCF program. Nevertheless, a gradient norm minimization method turned out to be most efficient in finally localizing the saddle points for the concerted dissociations of diimide. The reasons to hesitate before using gradient minimization are mainly two:

First, it is not a general method. It does not take one from the ends of the reaction to the desired activated complex. Practically all minimization algorithms will fail if the starting point is outside the region where condition ii) is valid. In practice this region can be very small. Second, it is costly. The second derivative matrix has to be constructed in some way.

Having these difficulties in mind, the case of dissociation of N_2H_2 was in the beginning approached in a quite different way. A reaction parameter was chosen, in most cases the N_2-H_2 distance or some function of it. The reaction was then driven along this parameter, with partial geometry optimization for the remaining degrees of freedom. When an energy maximum with respect to the reaction parameter was reached, a six point grid was laid out in the reaction parameter and one other coordinate, and a second degree polynomial was fitted in these points. The stationary point (saddle point) of this polynomial was then used as central point for another two-dimensional grid in another coordinate pair and so on. The procedure should go on until convergence.

Unfortunately the method did not work for the dissociations where the two hydrogens leave simultaneously. This was so despite of the limited number of degrees of freedom, three in C_{2v} and four in C_2. There is apparently a rapid change of the functional dependence of the true reaction coordinate on the internal coordinates over a wide area around the saddle point, and this is hard to mimic with the procedure outlined above. Both the N-N- and the H-H-distance change quickly for example, and these changes are strongly coupled. Attempts were made to change to coordinates which are less coupled. They were not successful. In C_{2v} one possible coordinate set is $(r_{N_2-H_2}, r_{HH}, r_{NN})$. The set $(r_{NH}, \theta_{NNH}, r_{NN})$, for example, had the same bad behaviour.

In another trial the choice of coordinate pairs for the polynomial fits was changed. After each fit a 2×2 second derivative matrix was at hand. In an attempt to recouple the two chosen coordinates the coordinate pair in the fit was linearly transformed to the eigenvectors of this matrix. This new pair was then used together with the remaining coordinates in later polynomial fits. These successive coordinate transformations did not manage to set an end to the oscillations in the series of two-dimensional stationary points.

The first step in the search procedure, i.e. to get sufficiently near to the TS starting from reactants and products, was at this stage recognized as the weak point. In a paper by Müller and Brown [15] the authors present a method for location of saddle points by a constrained simplex optimization procedure. The method does not use any derivatives and is summarized in the following paragraph.

Given two points, P_1 and P_2, on a minimum energy path, a new point Q (a "valleypoint") lying approximately on this path may be generated between P_1 and P_2 by minimizing the energy on a hypersphere centered around the higher of the two points with the radius defined as a fraction $f<1$ of the distance $|P_1P_2|$. To locate a saddle point between two energy minima, one generates valleypoints of increasing energy, closing in on the saddle point from opposite sides. A fixed value of $f>0.5$ is used. When the number of coordinates increases the energy minimization on the hyperspheres has to be very efficient. The authors suggest Simplex optimization.

This algorithm has been applied on the diimide dissociation. Our experience is that the method is well suited to close in on the saddle point region along approximate reaction paths, but does not seem to be appropriate for the final search.

To this end we finally decided to use gradient norm minimization. The gradient and Hessian matrix were produced numerically at a starting point. After this the Newton-Raphson method was applied without updating the Hessian. Two different starting points were tried in C_{2v}. The procedure diverged, however, in both cases. This was also the experience in recent calculations on activated complexes of SiH_5^- using an SCF-Gradient program [9]. As a last resort we turned to the more sophisticated algorithms. The choice fell on a least-squares method constructed by Powell [16] and first applied in quantum chemistry by Poppinger [27], where a mixture of Newton and steepest descent iterations are used. The Hessian is updated from formulas due to Broyden [28]. This algorithm turned out to be sufficiently flexible and all the saddle points of the concerted dissociation described in the previous section were now found. The strong coupling and changing curvatures were confirmed by the succesively constructed Hessians. Convergence was achieved in about sixty energy calculations for each saddle point.

5. Conclusions

The diimide potential energy surface has been studied using CASSCF and contracted CI methods. The surface was found to be quite complex and, besides the various local minima, three different saddle points were also found. These saddle points were located only after a considerable effort including around sixty energy evaluations in each case. The construction of an exact numerical Hessian followed by accurate update procedures finally converged to the saddle points. The number of negative eigenvalues of the Hessian was checked in each of these points and only one of them was found to be a true transition state with only one negative eigenvalue. The barrier height of this transition state with respect to *trans*-diimide was found to be 61 kcal/mol after vibration corrections. Removing one hydrogen from *trans*-diimide costs 56 kcal/mol and the removal of the final hydrogen from N_2H, hydroazine, went over a barrier of 5 kcal/mol. The barrier height for the concerted dissociation is therefore very close to the sum of the energies required to remove the two hydrogens separately. The preferable mechanism for dissociation should therefore be a stepwise loss of one hydrogen at a time, even though the concerted dissociation is very close in energy. Another argument for the non-concerted dissociation is the very long H-H distance of 5.5 a.u. found for the concerted transition state.

Most of the presently calculated geometries and relative energies for the different local minima on the N_2H_2 potential surface agree fairly well with earlier reported values in the cases where a comparison could be made, except in one case. For the N-H bond energy in diimide the presently calculated value is 56 kcal/mol whereas the value given in Ref. [24] in a GVB-CI calculation is 70 kcal/mol. Part of this large energy difference of 14 kcal/mol can be attributed to different ways of correcting for size inconsistency in the CI-calculations. Whether the multi-reference Davidson correction used here or the retention of bondedness used in Ref. [24] is the most accurate way of estimating the unlinked cluster contribution has to be checked by future more accurate calculations.

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