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MO CALCULATIONS ON ELECTROPHILIC REACTIONS—II

THE ADDITION OF HYDROGEN TO METHYLENE, A CARBENE INSERTION PROCESS

H. KOLLMAR†

Battelle-Institut e.V., Frankfurt (Main), Germany

and

Max Planck Institut für Medizinische Forschung, Heidelberg

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Abstract— The addition of hydrogen to methylene, the prototype of methylene insertion reactions, is studied with a modified CNDO procedure. Carbene insertions proceed *via* non least motion processes. The two product orbitals are formed consecutively, each by a steady combination of an occupied and an empty orbital of the reactants. This principle determines the calculated reaction coordinate and leads to a concerted two step mechanism. The chemical consequences of the mechanism are discussed.

INTRODUCTION

THERE is an increasing interest in the MO theoretical study of the reactions of singlet carbenes, which proceed *via* non least motion processes.[1] Thus, the dimerization of methylene was studied with the EHT[1] and the CNDO[2] method. Very recently the insertion of methylene into C—H bonds was investigated with EHT,[3] CNDO[4] and MINDO[5] procedures. Another example is a MINDO/2 study on the rearrangement of cyclopropylidene to allene.[6]

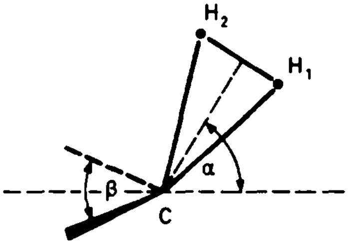

FIG 1. The geometrical parameters used in the calculation of the reaction coordinate (H_1 and H_2 are the atoms of the approaching hydrogen molecule; α is the angle between the methylene plane and the line bisecting the H_1CH_2 angle; β is the HCH angle of the methylene).

In this study the prototype of methylene insertion reactions, the addition of H_2 to CH_2, is investigated with a modified CNDO procedure in order to reveal the electronic factors which determine the reaction coordinate.

Computational methods

1. *The modified CNDO method.* The MO method used in this study is a modified[7]

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† Present address: Dept. of Chemistry, University of Texas, Austin, Texas 78712

CNDO procedure[8] which yields in general reasonable heats of atomization together with satisfactory equilibrium geometries for hydrocarbons, hydrocarbon radicals[9] and carbonium ions.[10] In the case of hydrocarbons, the computed heats of atomization deviate normally less than 2 percent from the experimental values. An exception are strained-ring compounds which come out too stable by about 0·04 a.u. per ring. The computed bond lengths and valence angles are generally within 0·02 Å and 3°, respectively, of the experimental values. Thus, the method allows a complete minimization of the energy of a molecular system with respect to its geometry. This property of the method is imperative for a MO study of reaction coordinates.

2. *Energy partitioning method.* Within the CNDO formalism the total energy of a molecular system can be broken down into mono and bicentric terms,[11] *i.e.* the energy can be ascribed to atoms and bonds:

$$E = \sum_{A} E_A + \sum_{A>B} E_{AB}$$

The energy terms of the bonds can be further partitioned into physical components. The most important is the bond resonance energy E^R_{AB}, defined by

$$E^R_{AB} = 2 \sum_{\mu \epsilon A} \sum_{\nu \epsilon B} \beta_{\mu\nu} P_{\mu\nu} S_{\mu\nu}$$

which can be regarded as an energy-weighted overlap population. As has been shown in detail,[10] the values of E^R_{AB} as well as of E_{AB} are measures of the strength of the bond A—B. Thus, it is possible to use the values of these quantities as indicators for bond breaking and bond formation along a reaction coordinate.

3. *MO transformations.* As is well known,[12] the canonical SCF orbitals can be subjected to an arbitrary orthogonal transformation without changing the expectation value of any operator.

A special orthogonal transformation of the MO's leads to the localized orbitals.[13] The procedure of transforming the MO's of a CNDO calculation to the corresponding localized orbitals using the principle of minimum interorbital exchange energy was first used by Trindle and Sinanoglu.[14] In this study, we used the transformation to localized orbitals in order to separate the two C—H bond orbitals of the original methylene which do not change essentially during the reaction. The two remaining orbitals corresponded to two three-centre bonds or to two distinct C—H bonds, depending on which point of the reaction coordinate is regarded. In order to get a uniform type of orbital along the whole reaction coordinate, these two orbitals were transformed orthogonally to an approximately symmetric and an antisymmetric orbital with respect to the H—H bond.

The calculated reaction coordinate

The ΔH_0 of the reaction is calculated to be 87 kcal/mole compared with an experimental value of 111 kcal/mole[15] (at 25° without a correction for zero point energy).

The interesting part of the energy hyperplane was obtained in the following way: For different given C—H distances the H—H distance was varied over a large range (0·7 to >2 Å), while two other geometrical parameters, the angle α between the methylene plane and the plane bisecting the approaching hydrogen molecule and the H—C—H valence angle β (Fig 1), were optimized. Thus, the energy of the system resulted as a function of the H—H distance for different C—H distances as

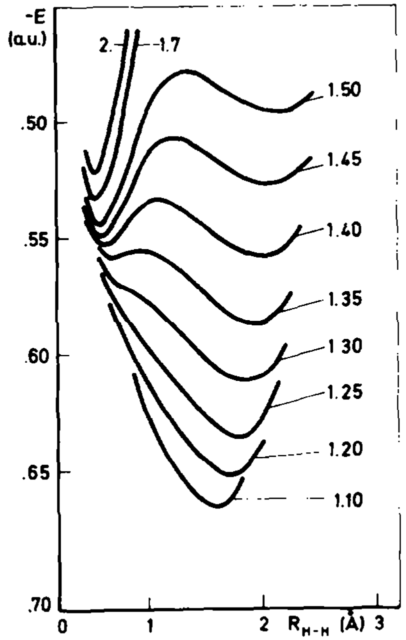

FIG 2. Total energy as a function of the H—H distance for different C—H distances.

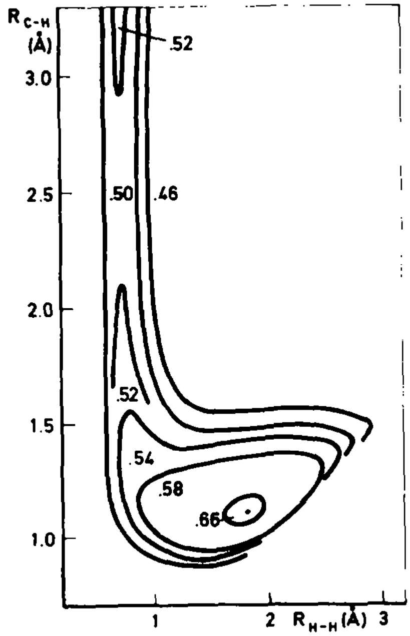

FIG 3. Energy contour map for the system $CH_2 + H_2$.

shown in Fig 2. From these curves the energy contour map of Fig 3 could be constructed. It is noteworthy that there are two energy minima for given C—H distances greater than 1·30 Å, one with a short H—H and the other with a long H—H distance. For the minima with the short H—H distance, the optimum values for the angle α as a function of the C—H distance are given in Fig 4.

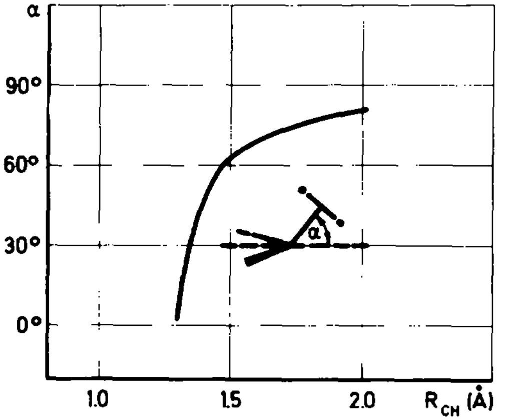

Fig 4. Optimum values for α as a function of the C—H distance.

For the minima with the large H—H distance, the angle α comes out to be zero throughout. For the short H—H distances, the angle β increases from the value in methylene (120°) up to a value of 130° for a C—H distance of 1·30 Å. At the same C—H distance and the longer H—H distance the value for β is much smaller (116°).

The following picture of the reaction coordinate is obtained from these results.

The reaction proceeds in two fairly well separated steps:

1. The empty p orbital of the methylene approaches the hydrogen molecule forming a three centre bond. The transition state for the reaction is reached at a C—H distance of 2·45 Å. The corresponding activation energy is calculated to be not more than 5 kcal/mole. Since in this phase the methylene valence angle is somewhat enlarged it is expected that the reaction will not be hindered by bulky substituents at the methylene.
2. In the second phase of the reaction the H—H distance is enlarged rapidly, while α goes to zero and β decreases to 110°, thus reaching the final tetrahedral geometry.

These results are qualitatively analogous to those obtained for the insertion of methylene into the C—H bond of methane with EHT calculations.[1]

In the first phase of the reaction (with $\alpha \neq 0$) the two hydrogen atoms H1 and H2 are not equivalent. However, in our calculations the two bond lengths C—H1 and C—H2 were assumed to be equal throughout. In the case of a C—H bond length of 1·70 Å, the effect of this restriction was tested. After geometry optimization with the restriction, the energy was minimized within the more flexible restriction that the arithmetic mean of the two C—H bond lengths be 1·70 Å (unrestricted minimization would lead to the methane structure). This procedure yielded the values of 1·61 and 1·79 Å for the C—H1 and C—H2 bond lengths respectively, while the energy of the system was lowered by not more than 0·25 kcal/mole. Thus, the restriction C—H1 = C—H2 has no serious consequences for our study.

An interesting consequence of the double minima character of the curves of Fig 2 should be mentioned. One could construct the reaction coordinate for the elimination of H_2 from methane in the following way: One increases two C—H bond lengths in methane step by step, optimizing all the other geometrical parameters each time. In this manner, one would pass through the energy minima with the long H—H distance (Fig 2), thus missing the minimum energy path and obtaining the forbidden symmetrical one. This example demonstrates how cautious one must be in calculations of reaction coordinates.

In the following sections the electronic factors responsible for the two-step mechanism of carbene insertions are investigated in detail, in order to evaluate the chemical consequences of the mechanism.

Population and energy partitioning analysis

During the first phase of the reaction (CH $\geqslant$ 1·45 Å), in which the hydrogen molecule approaches the empty p orbital, a 3-centre bond is formed. Consequently, a charge transfer occurs from the hydrogen molecule to the C atom. The populations of the H atoms of the H_2 (Fig 5) do not fall below 0·89. Thus, the gross charge transfer does not exceed 0·22 elementary charges. At the same time, the bond order between the two hydrogen atoms decreases smoothly from 1 to 0·8 (Fig 5). The behaviour of the bond strengths as reflected in the resonance energy (E^R) values, is quite analogous. E^R decreases for the H—H bond, but increases smoothly for the (newly formed) C—H bonds for decreasing C—H bond lengths (Fig 6).

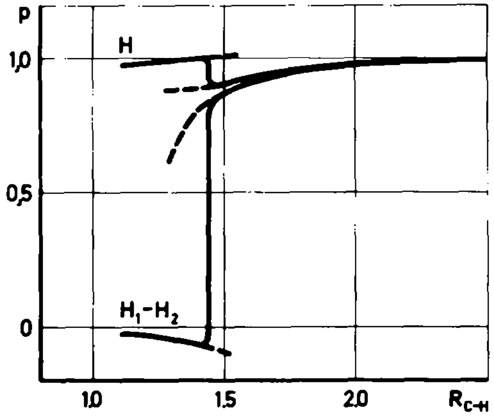

FIG 5. Charge density (P_H) and bond order (P_{H1H2}) in the approaching H_2.

As mentioned before, the two hydrogen atoms (H1 and H2 in Fig 1) of the approaching hydrogen molecule are not equivalent in the first phase of the reaction. At a CH distance of 1·70 Å the populations of H1 and H2 are slightly different (0·941 and 0·951 resp.). The C—H1 is somewhat stronger (E^R = −0·084) than the C—H2 bond (−0·075). Figs 5 to 7 show the arithmetic mean of the values of the two hydrogens.

The second phase of the reaction is characterized by a rapid fall-off of the H1—H2 bond order (Fig 5) and of the corresponding resonance energy (Fig 6), while the C—H bond strength increases fairly steadily during both reaction phases. Obviously, the reaction coordinate is determined mainly by this quantity.

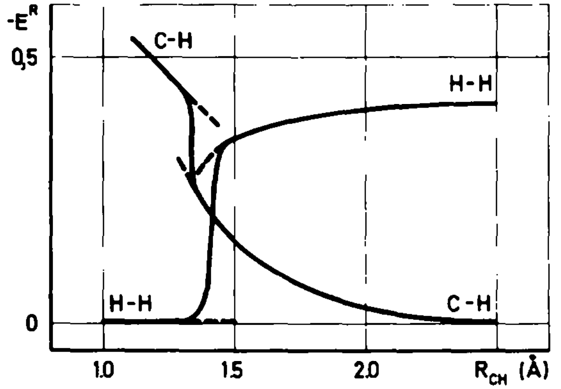

FIG 6. Resonance energies of the C—H and the H_1—H_2 bond as a function of the CH distance.

Finally, the transition between the two energy minima (Fig 2) occurring at two H—H distances for the given C—H distance of 1·40 Å is regarded. In this case, an increase of the H—H bond length leads to an steady decrease of the H—H bond energy, while the CH resonance energy is increasing at about the same rate (Fig 7).

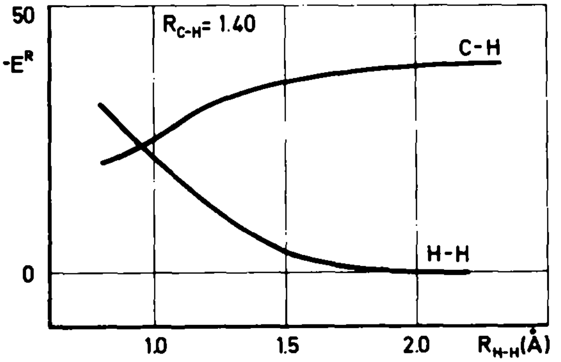

FIG 7. Resonance energies of the C—H and the H_1—H_2 bond as a function of the H_1—H_2 distance (for C—H = 1·40 Å).

These curves of the resonance energies show no indication of the double minima characteristic of the corresponding energy curve (Fig 2). The barrier separating the two minima is mainly due to rehybridization effects.

The orbitals involved

Since the two CH bonds of the original methylene remain essentially unaffected during the insertion process, only two occupied orbitals are left which are involved in the reaction. In the reactants, these two orbitals are the hydrogen σ bond orbital and the lone pair of the methylene. In the product, the two localized orbitals of the C—H bonds formed during the addition process can be represented by two three-centre orbitals as is shown in Fig 8. The first one (φ_1) forms a three-centre bond, while the second one (φ_2) is antibonding for the H—H bond.

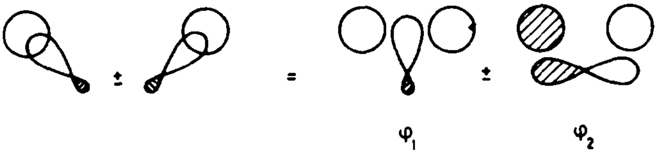

FIG 8. Representation of two localized C—H bonds as a linear combination of two three-centre orbitals.

1. In the first phase of the reaction a steadily increasing amount of the empty p orbital is mixed into the bonding orbital of the hydrogen molecule and a 3-centre bond is formed. Thus, charge is transfered from the hydrogen bond to the empty orbital of the methylene. In Fig 9 the gross charge transfer is broken down into a transfer from the hydrogen σ bond to the carbene C atom and a backdonation from the C atom to the σ^* orbital of H_2 (calculated from the coefficients of φ_1 and φ_2, resp.). Due to the weak basicity of H_2, the charge donation from the H_2 molecule connected with the forming of the three-centre bond does not exceed 0·25 elementary charges even at a distance as short as 1·50 Å. At that distance a small amount of back donation of charge from the methylene lone pair to the σ^* orbital of H_2 is observed. The geometry of the first phase of the reaction is the optimal arrangement for the building up of a three-centre bond. At distances below 1·5 Å the back donation of charge lowers the angle α of Fig 1. (Fig 4).

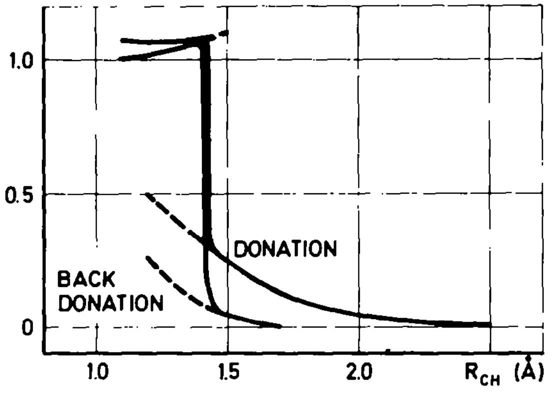

FIG 9. Break down of the charge transfer as a function of the C—H distance.

The first phase can be called the electrophilic step of the reaction. This part of the reaction is comparable with the electrophilic addition reaction of carbonium ions as they are observed in super acid media.[16] The prototype of this reaction, the addition of the CH_3 cation to hydrogen forming the CH_5 cation, has been calculated with the modified CNDO method.[17]

While the first phase of the reaction is a pure addition process, the second phase contains another characteristic of an insertion: the bond breaking in the substrate.

2. In the second phase of the reaction the antibonding orbital of H_2 is mixed to the lone pair orbital of the methylene and the three-centre orbital φ_2 (Fig 8) is formed. Thus a back donation of charge from the C atom to hydrogen molecule occurs. The population of the σ^* orbital of H_2 is reflected in the reaction coordinate by the rapid increase of the H—H bond distance. This phase of the reaction can best be studied by fixing the C—H bond distance at 1·40 Å and enlarging the H—H bond distance from 0·84 Å, the value belonging to the first energy minimum (Fig 2), to 2·20 Å (second energy minimum). During this process the σ^* orbital of H_2 is populated steadily (Fig 10). However, the σ orbital of H_2 is depopulated at about the same rate (Fig 10). This remarkable electronic reorganization during the enlarging of the H—H bond distance is accompanied with an activation energy of not more than 12 kcal/mole. Thus, the reaction coordinate is highly flexible.[1]

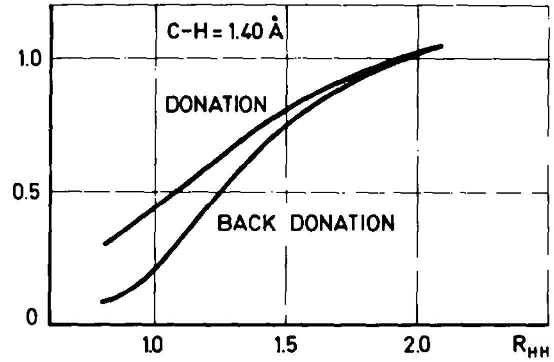

FIG 10. Break down of the charge transfer as a function of the H—H distance (for C—H = 1·40 Å).

The second phase of the reaction may be called the nucleophilic step of the insertion process, since the lone pair of the methylene participates in this phase.

A reaction will proceed with low activation energy if occupied and empty orbitals are mixed steadily along the reaction coordinate. As we have seen, the path of the methylene insertion process is clearly determined by this principle.

CONCLUSIONS

In this section the principle chemical consequences of the steric and electronic factors determining the carbene insertion process shall be discussed.

1. The geometry of the transition state of carbene insertion reactions is very different from the product structure. Because of the three-centre bond there are small valence angles in the transition state. Thus, strained systems can be obtained by carbene insertion processes. Experimentally, numerous examples of this type are known.[18,19]

2. From the steric requirements of the transition state it is clear that insertion reactions into σ—C—C bonds are sterically hindered.[3,4] Thus no intermolecular insertion reactions of carbenes into C—C single bonds are known. However, this restriction is not valid for linear carbenes (such as the vinyl cation, which can be regarded as a CH_2 substituted methylene).[20]

3. Bulky substituents of the methylene should not effectively hinder the insertion process, because the methylene valence angle does not decrease but, indeed, increases somewhat in the first phase of the reaction.

4. The insertion reaction can be hindered by lowering the electrophilicity of the empty carbene p orbital. An example is cyclopropenylidene. The reverse process, the α elimination from cyclopropene, should also be hindered, though the carbene should be fairly stable thermodynamically.

5. The insertion process cannot be hindered by lowering the nucleophilicity of the carbene lone pair, because the second phase of the reaction is not rate determining. An extreme example is again the vinyl cation, which, according to MO calculations[20], should undergo insertion reactions easily.

6. It might be possible to modify the system in such a way that an intermediate (corresponding to a local minimum) is formed after the first step of the reaction. In this case, there would be an energy barrier for the second phase of the reaction. Such a modification could be accomplished either by lowering the nucleophilicity of the methylene lone pair with acceptor substituents, thus hindering the second phase of the reaction, or by increasing the donor capability of the substrate bond, thus favoring the first stage of the reaction. However, calculations on the vinyl cation + H_2 system[20] demonstrate that strong electron accepting substituents on methylene are not sufficient in order to obtain such a double minima reaction coordinate.

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