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PMO ANALYSIS OF CYCLOADDITIONS[1]-II. THE TRANSITION STATE OF THE ADDITION OF FORMONITRILE OXIDE TO ACETYLENE

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Abstract: Perturbation calculations on the transition state of the reaction of formonitrile oxide (fulminic acid) with acetylene are reported. The energy partitioning in covalent and non-covalent contributions reveals that the type II behavior of formonitrile oxide which is expected according to the classification scheme of cycloadditions is observed only if distortions of the molecules as in the ab-initio calculated transition state structure are taken into account. The results support unequal bond formation with a preference for the CC bond.

Introduction

As one of the prototypes of 1,3-dipoles, formonitrile oxide has found attention several times in theoretical investigations. Elaborate ab-initio[2-5] and semiempirical[6] calculations have been carried out to answer the question of concertedness in the cycloaddition of this 1,3-dipole to acetylene and to determine the structure of the transition state. Although no unanimous conclusion has been obtained as far as the one- or two-step mechanism is concerned, the concerted pathway seems to be favored[7]. Our analysis will be based on the transition state for the concerted reaction, in particular on that reported in ref. 3.

The experimental studies on cycloadditions of formonitrile oxide[8] and substituted nitrile oxides[9-12] are in agreement with a synchronous mechanism. Frontier molecular orbital theory has proved successful in explaining reactivity[13] and regioselectivity[7,14] for 1,3-dipolar cycloadditions. According to the classification scheme for (4 + 2) cycloadditions[13], formonitrile oxide and its derivatives belong to type II, i.e. they show enhanced reactivity towards both electron deficient and electron rich olefins.

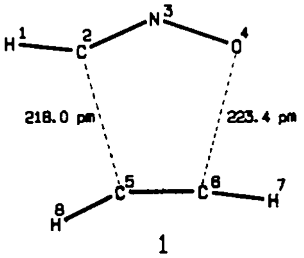
Calculational Procedures

The recently developed perturbation program PERVAL[1] based on the MINDO/3 formalism[15] is used for the calculations. The aim of this program is the improvement of solely π-electron based perturbation procedures like FMO theory or more sophisticated second order perturbation treatments. A proper treatment of covalent-, non-covalent and charge interactions requires at least a semiempirical valence electron theory[16,17]. We make use of the MINDO formalism in order to make the program applicable to larger systems which are not accessible to ab initio treatments. If such a program is to be applied widely it should also run on a small computer. Therefore, we have programmed the perturbation formalism[16,17] for an IBM AT personal computer. In calculating the interaction of two molecules we generate the MINDO/3 wave functions with the personal computer and combine these, together with the information on the structure of the molecular complex, to an input file for the perturbation program. The results are displayed graphically and are evaluated interactively. At present we can deal with complexes of two molecules where each may have a basis set of up to 60 valence orbitals.

Results

The calculations are based on the geometries for formonitrile oxide and acetylene of ref. 3. Besides molecular complexes of the 1,3-dipole and acetylene in the undistorted structure **2** we analyze the transition-state structure **1** which was determined by ab-initio calculations[3].

First we considered the undistorted structures of formonitrile oxide and acetylene. The reaction is assumed to be symmetric with respect to the reactive centres. The perturbation evaluation was done on complex **2** at separations r of 250 and 225 pm. In order to show the quality and applicability of our perturbation treatment we report in Table 1 not only the perturbation energies up to second order but also the total energy of the molecular complex **2**, calculated as supermolecule by the MINDO/3 method. It is satisfying that even at a distance of 225 pm the deviation of the heat of formation of **2** from the sum of these values for formonitrile oxide and acetylene plus the perturbation energy is only 0.6 %. A priori it was not obvious that a perturbation formalism of this kind can be applied successfully at distances which are similar to those in the calculated transition state **1**.



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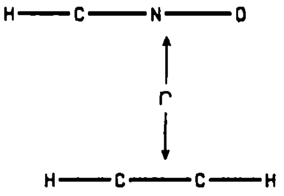

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Table 1 shows that the effective first-order energy which includes the nuclear repulsion[17,18] is repulsive as expected. This energy contribution can be separated into a term which describes polar interactions due to the net atomic charges of the constituent atoms and a term which is similar to the closed shell

Table 1: Perturbation and MINDO/3 energies for complexes **1** and **2**, the components formonitrile oxide and acetylene (kcal/mol).

	ΔH_f	1st.order		2nd order	sum[a)]
	MINDO/3	polar	non-covalent		
formonitrile oxide[b)]	12.86				
acetylene[b)]	58.25				
formonitrile oxide[c)]	25.22				
acetylene[c)]	65.48				
2	93.03[d)]	-0.62	26.43	-3.53	93.38
2	108.16[e)]	-0.87	47.85	-9.26	108.83
1	107.61	-0.21	43.63	-24.12	110.00

a) ΔH_fFormonitrile oxide + ΔH_facetylene + 1st. order + 2nd. order; b) undistorted, bond lengths acc. to ref. 3; c) structures acc. to **1**, see ref. 3; d) separation 250 pm; e) separation 225 pm;

repulsion in one electron treatments. The latter amounts to almost all of the first-order energy, i.e. even though formonitrile oxide is a polar molecule, this property does not cause appreciable repulsion or attraction between the molecules. The value of the closed shell repulsion can be split further into contributions from individual atoms or specific atom pairs. In this way, we find at a distance of 250 pm that the carbon atom of acetylene which reacts with the oxygen atom of formonitrile oxide shows a total repulsion of 8.4 kcal/mol and and a repulsion of 2.6 kcal/mol to the oxygen atom alone. For the carbon atom forming the CC bond, we observe a total repulsion of 11.8 kcal/mol and a repulsive interaction of 6.8 kcal/mol with the C atom of formonitrile oxide. Therefore, we conclude that due to the higher repulsion of the carbon atoms as compared to the carbon-oxygen pair the transition state for the two reactants should not be symmetrical. On the basis of purely non-covalent interactions, the CC approach should be less favorable.

It is of interest to see whether the second-order energy, which results from the interactions of filled orbitals of one molecule with empty ones of the other and which includes the FMO-contributions, reproduces the expectation from the reactivity model[13] . For formonitrile oxide as a type II 1,3-dipole, we should find similar amounts of stabilization from both HOMO - LUMO interactions. In table 2 we list these values for the interactions of the π-orbitals of the 1,3-dipole, which extend in the direction of acetylene, with the unoccupied ones of acetylene, which point to formonitrile oxide, and vice versa (notation according to Fig. 1). There is negligible stabilization from the π-orbitals perpendicular to the plane of the complex **2**.

Table 2: Second order interaction energies of π- and π*-orbitals in **1** and **2** (kcal/mol); notations see Fig. 1 and 2.

	separation (pm)	$\Pi_1-\Phi_2$	$\Pi_2-\Phi_2$	$\Phi_1-\Pi_3$	$\Pi_1-\Phi_3$	$\Pi_2-\Phi_3$
2	250	<0.001	-1.54	-0.05		
2	225	<0.001	-3.98	-0.17		
1		-0.04	-6.48	-8.20	<0.001	-2.70

It is astonishing to note that only one FMO interaction is appreciable, that of $HOMO_{HCNO}$ with $LUMO_{HCCH}$. The other energies are smaller by an order of magnitude. This failure with respect to the expectation from the experimental results on nitrile oxide cycloadditions implies either that the perturbation treatment is unsatisfactory or that our model of the transition state is incomplete.

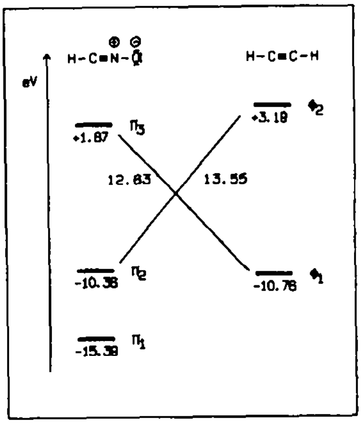


Fig.1: π-Orbital diagram for linear formonitrile oxide and acetylene according to MINDO/3

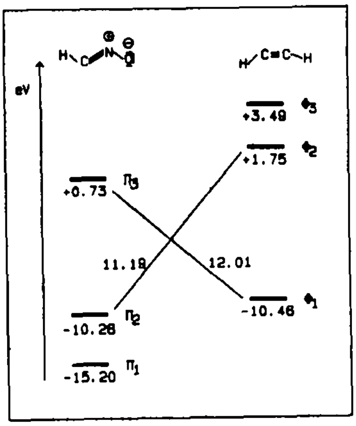
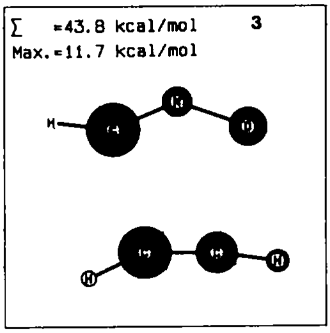


Fig.2: π-Orbital diagram for bent formonitrile oxide and acetylene according to MINDO/3

The calculations on the undistorted molecules indicate that the perturbation treatment can be applied even at separations of the reaction partners of ca. 225 pm. Therefore, we investigated the <u>ab-initio</u> transition state **1** with the perturbation program PERVAL. The complex **1** was separated into formonitrile oxide and acetylene. For both distorted molecules we carried out MINDO/3 calculations and used the resulting wave functions to calculate the interaction of the molecules in the structure of the transition state 1. The results are presented in Table 1, where the sum of the heats of formation of bent formonitrile oxide, acetylene and the perturbation energy are compared with the heat of formation from the MINDO/3 calculation of the transition state. Although the perturbation at the transition state must be sizable, our treatment reproduces the total energy surprisingly well. This result could not be foreseen and it disproves the opinion[5] that perturbations at the transition state should be too big in order to apply perturbation theory. Therefore, we can proceed to analyze the individual energy components. Polar interactions are negligible, non-covalent repulsions are twice as high as the second-order stabilization.

For C-6 (see 1) we find a share of 14.4 kcal/mol of the total 43.6 kcal/mol describing the non-covalent repulsion with formonitrile oxide. 7.1 kcal/mol of this value derive from the interaction of C-6 with the oxygen atom (O-4). The fraction stemming from C-5 is 23.2 kcal/mol. The carbon atom of formonitrile oxide contributes 17.9 kcal/mol to this value. In 3 we display a pictorial representation of the contributions of the individual atoms to the total repulsion. 4 and 5 show the partitioning of the repulsions of C-5 and C-6 with formonitrile oxide in contributions from individual atoms. The area of the circles is used as measure of the amount of interaction. The picture which emerges from this analysis is in accordance with that derived from the perturbation calculations using the ground state structures of formonitrile oxide and acetylene. It is easier for the oxygen atom of formonitrile oxide to approach acetylene than for the carbon atom.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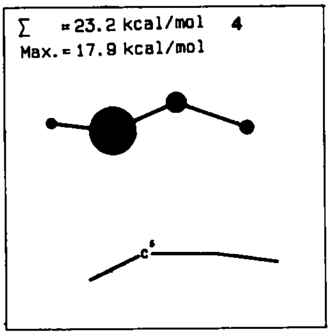
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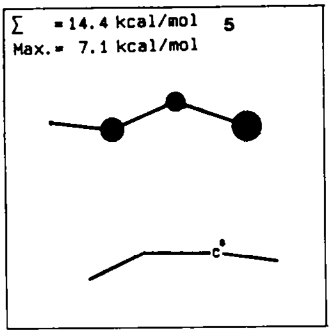
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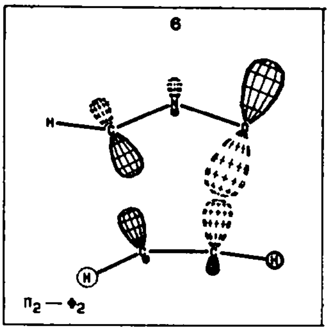
The separation of the second-order perturbation energy in the transition state 3 into individual components shows dramatic differences between the transition state model 1 and the model of the undistorted molecules (2). We recognize now a similar influence of <u>both</u> FMO-interactions (Table 2, fig. 2). Second-order energies of -6.5 kcal/mol and -8.2 kcal/mol are provided by the $HOMO_{HCNO}$ - $LUMO_{HCCH}$ and $HOMO_{HCCH}$ - $LUMO_{HCNO}$ interactions, respectively. In addition, we see that a second interaction of $HOMO_{HCNO}$ with an unoccupied MO of acetylene has a sizable value. The sum of the three interactions amounts to 72 % of the total second order energy. This underlines the importance of the frontier molecular orbital interactions for the stabilization of the transition state of this cycloaddition. The similarity of both HOMO-LUMO interactions is in agreement with the experimental observation that nitrile oxides belong to type II of the classification (see above). The comparison of this result with that for the reactants in their ground state structure demonstrates that it might be dangerous to interpret intermolecular interactions without considering structural changes in the molecules.

6



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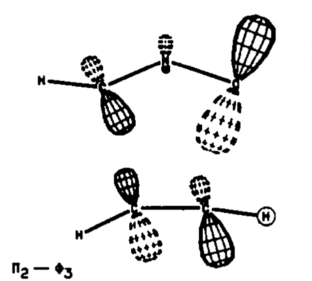

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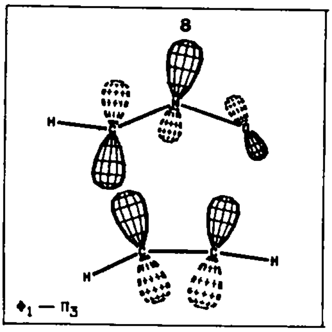

What are the structures of the relevant MOs of formonitrile oxide and acetylene and what is the reason that there is such a remarkable difference in behavior between complexes **1** and **2**? An answer can be found in representations **6** - **8** where we display the structures of the orbital pairs together with their notation according to Fig. 2. The drawings are produced by our perturbation program which automatically forms hybrid orbitals from the s- and p-AOs.

In **6** and **7** $\text{HOMO}_{\text{HCNO}}$ interacts with unoccupied MOs of acetylene. As a consequence of the bent structure of acetylene there are now two antibonding empty orbitals of π-nature and appropriate symmetry. The reason for the greater stabilization in **6** as compared to **7** can be recognized easily. The bending of formonitrile oxide and acetylene causes a rehybridization of the atoms and a directional adjustment of the orbitals. They acquire some s character, making them unsymmetrical, and now the bigger lobes point into the direction of the new bonds. The smaller stabilization in **7** can be attributed to a slightly bigger orbital energy separation and to the different size of the orbital lobes of the unoccupied MO of acetylene pointing towards formonitrile oxide. Also, the colinearity of the AOs participating in the CO bond is not provided.

$\text{HOMO}_{\text{HCCH}}$ interacts with the LUMO of formonitrile oxide which has the same phase distribution as the LUMO of the allyl anion. As the $\text{HOMO}_{\text{HCCH}}$ perfectly matches this MO we can understand that this interaction is as important as that in **6**. However, there is one more aspect to be discussed. Whereas in **6** the amount of interaction between the reacting atoms seems to be similar the carbon - oxygen interaction is disfavored in **8**. From this we can delineate that the CC bond formation in the transition state is preferred over CO bond formation. This is in accordance with the conclusions from the ab-initio calculation of the transition state^1 but in disagreement with Streitwieser's charge-density analysis^5 . The comparison of the CC and CO distances in the transition state **1** and in the final product^3 provides additional support. The CO bond has not as far progressed as the CC bond. This might indicate that the aforementioned less favorable repulsive interaction between the reactive carbon atoms does not influence the bond building process significantly.

It is important to analyze whether the comparable big FMO contributions in *6* and *8* are a consequence of changes in the orbital energy separations or whether they arise from other effects. In Fig. 2 we present the energy level diagram of the occupied and unoccupied MOs, shown in *6* - *8*. The comparison of fig. 1 with fig. 2 tells us that the difference in stabilization cannot be caused by a change in the energies of the MOs alone. An increase of the value of the numerator of the FMO expresssion must also be made responsible. Two sources can be found for this effect which can both be derived from *8*. The rehybridization leads to a better overlap of the orbitals involved in the bonding process and the bending of formonitrile oxide moves the nitrogen atom away from the double bond. This decreases the antibonding interaction between nitrogen and the orbitals of the double bond.

The program PERVAL allows us to represent pictorially the amount of covalent interaction between atoms of the two molecules K and L resulting from a particular orbital combination, for instance a HOMO and LUMO pair. This corresponds to an analysis of the numerator of the expression for the second order stabilisation for individual molecular orbital pairs[1]. Two different values can be displayed which are calculated according to eq. 1 or eq. 2:

$$\Delta E^{kl}_{up} = \sum_{\kappa}\sum_{\lambda} c_{u\kappa}\, c_{p\lambda}\, \beta_{\kappa\lambda} \qquad \text{eq.1}$$

$$\Delta E^{m}_{up} = -1/2 \sum_{n}\left(\sum_{\kappa}\sum_{\lambda} c_{u\kappa}\, c_{p\lambda}\, \beta_{\kappa\lambda}\right) \qquad \text{eq.2}$$

Here, $\beta_{\kappa\lambda}$ is the resonance integral between orbitals κ and λ of atoms k and l and $c_{u\kappa}$ resp. $c_{p\lambda}$ are the eigenvector coefficients of the AOs κ and λ in the MOs u and p. For the orbital pair u (occupied) and p (unoccupied) the indices κ and λ run over the AOs of the atoms k and l of molecules K and L. Thus, ΔE^{kl}_{up} corresponds to an orbital pair related interaction between atoms k and l. In eq. 2, we sum up the interaction of an atom m of K or L with all the atoms n of the other molecule. The factor 1/2 takes care of the fact that we count each interaction twice, considering once the interaction from molecule K and then also from L. The sign of individual ΔE^{kl}_{up} or ΔE^{m}_{up} values may be either positive or negative depending on the sign of the eigenvector coefficients. In the calculation of the interaction energy of the orbital pair, the sum of the ΔE^{m}_{up} values is squared, divided by the excitation energy and multiplied by -2[1].

The result is enlightening. For Π_2-Φ_2 (*6*) and Φ_1-Π_3 (*8*), we display the ΔE^{m}_{up} values in **9** and **10** where the area of the circles indicates the magnitude of the values. The four atoms involved in the formation of the two new σ-bonds provide ΔE^{m}_{up} values of equal sign, i.e. they are responsible for the strong bonding interaction of Π_2-Φ_2 and Φ_1-Π_3. The central nitrogen atom, having a ΔE^{m}_{up} value of opposite sign, counteracts the stabilization of $HOMO_{HCCH}$-$LUMO_{HCNO}$. From the size of the circles at the reactive centers we can deduce that both HOMO-LUMO interactions favor CC bond formation. In **11** and **12** we show how the ΔE^{m}_{up} values in the representation *9* are assembled from individual ΔE^{kl}_{up} contributions. The small circle at C-6 in *9* as compared to C-5 originate from bonding (C-6-O-4) and antibonding (C-6-N-3 and C-6-C-2) portions. This compensating effect is less

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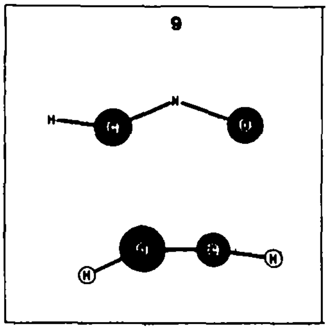

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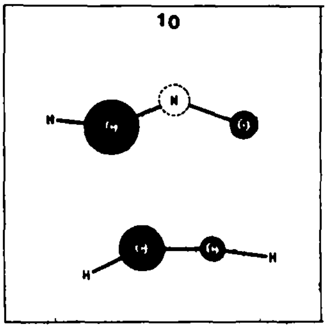

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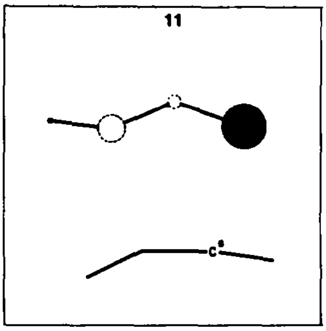

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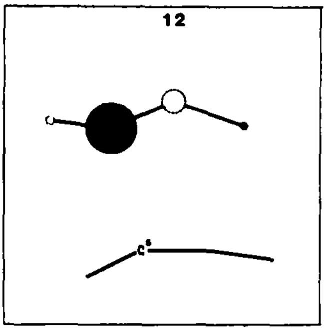

important in the interaction of C-5 with the nitrile oxide (12). We must conclude that CC bond formation is favored over CO bond formation. Qualitatively, this conclusion was already reached from an inspection of complexes 6 - 8. It should be emphasized that we do not try to distinguish between a one- or two-step mechanism for the cycloaddition by this analysis, i.e. a concerted-, diradical- or ionic pathway. Our perturbation procedure can only recognize salient features of the interaction. In this case it tells us that the two reacting molecules do not form the two new bonds to the same degree at all stages of the reaction path. Whether this might result in a two-step mechanism cannot be decided on the basis of the perturbation treatment. As the elaborate calculations by Hiberty et al.[4] demonstrate, the one-step or the two-step reaction may be very close in energy making a decision between these possibilities a delicate problem. In such a case solvation effects might also have a significant influence. However, our analysis is in full agreement with the unsymmetrical transition state 1 which accounts for the concerted reaction.

Conclusion

From the present study we may draw several conclusions. Perturbation theory can provide valuable information on the energy components which determine the structure of the transition state of the cycloaddition of formonitrile oxide to acetylene. For future applications it will be important to keep in mind that a PMO treatment based on undistorted structures of the reactants may not be very meaningful in all cases. Our analysis furnishes a possible procedure to circumvent this problem. If the perturbation calculations are generally possible at distances and with structures which are obtained from ab-initio or other calculations for transition states then one might combine both approaches. Studies on problems of reactivity and regioselectivity in nitrile oxide cycloadditions[20] and in diazomethane cycloadditions[21] indicate that it is not necessary to carry out elaborate calculations for each reactant pair. The transition state structure for the parent pair where hydrogen atoms are replaced by substituents can be used successfully.

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