Reaction of Imidazoles with Ethylene and Singlet Oxygen. An ab Initio Theoretical Study

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The structures of the three possible tautomers of imidazole were optimized with the MP2/6-31G* theoretical model, and their relative energies were compared. All possible transition structures for the Diels−Alder reaction between the imidazole tautomers as dienes and ethylene and oxygen as dienophiles were generated at the RHF/3-21G and RHF/6-31G* level of ab initio molecular orbital calculations. The activation energies were also evaluated at the MP3/6-31G*//RHF/6-31G* level. One transition structure for the ethylene addition to the most stable imidazole isomer was also generated at the MP2/6-31G* level, and single point energies calculated on the structure were compared to the ones obtained on RHF/3-21G and RHF/6-31G* geometries. The structures correspond to concerted but not necessarily synchronous cycloadditions. The synchronicity of the reactions is discussed on the basis of the bond orders of the new forming bonds in the transition states. Also, on the basis of the bond orders qualitative predictions of the reactivity of the different imidazole tautomers can be made. The quantitative order of the reactivity was obtained by comparing the activation energies for the ethylene and oxygen additions to the imidazole tautomers. It was concluded that imidazole is not a particularly suitable diene for cycloaddition reactions because its HOMO energy is too low and LUMO energy is too high for efficient molecular orbital overlap. This is due to the aromatic stability of the imidazole ring and the presence of the nitrogen lone pair orbital very close to the reactive centers which increases the energy of the transition structures through repulsions of the filled orbitals. Because of this interaction it is predicted that the products of the cycloaddition reactions, if formed, will be from imidazole tautomer **1**.

Introduction

An interesting problem in heterocyclic chemistry is the high unreactivity of imidazoles and their derivatives as dienes in cycloaddition reactions. Usually the reaction does not lead to the expected Diels−Alder adduct, but to a product of N-alkylation, such as in the case of dimethyl acetylenedicarboxylate.[1] Nevertheless, there are instances in which some form of addition takes place. The imidazole ring must have strong electron-withdrawing substituents giving rise to inverse electron demand Diels−Alder cycloadditions, where the imidazole LUMO is involved.[2] Another way to involve the imidazole ring in Diels−Alder reactions is by its transformation into mesoionic imidazole. For instance, these compounds, in reaction with activated acetylenes through Diels−Alder adducts, give derivatives of pyrroles.[3]

Singlet oxygen reacts very slowly with imidazole and forms imidazolidinone through the Diels−Alder adduct which later involves an elimination reaction with proton loss of the peroxide adduct. This reaction is responsible for the photooxidative enzyme inactivation through the hetero Diels−Alder addition of oxygen to histidine in the active enzyme pocket.[4]

We report here the results of a theoretical study of the Diels−Alder reaction of imidazole tautomers with both ethylene and oxygen as representatives of carbon and hetero cycloadditions.

Computational Methodology

The initial search for the transition state structures was performed on a DEC 7620 computer with the MOPAC[5] PM3[6] method. The obtained structures were optimized on a Silicon Graphics Personal Iris computer at the RHF[7] /3-21G[8] and RHF/6-31G*[9] levels with the Gaussian 92[10] program. The energy was evaluated at the third-order Møller−Plesset perturbation theory[11] and the 6-31G* basis set level. The geometries of all three possible tautomers of imidazoles were also optimized with the MP2/6-31G* theoretical model. All the reactants are minima on the potential energy surface with all positive eigenvalues, and the transition state structures[12] have only one negative eigenvalue and, therefore, one imaginary frequency. The normal coordinates of the imaginary

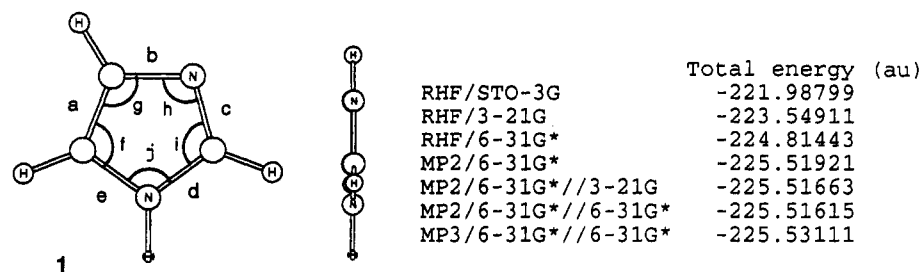† Permanent address: Institute of Chemistry, Cyril & Methodius University, Arhimedova 5, Skopje, Macedonia.

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	Total energy (au)
RHF/STO-3G	-221.98799
RHF/3-21G	-223.54911
RHF/6-31G*	-224.81443
MP2/6-31G*	-225.51921
MP2/6-31G*//3-21G	-225.51663
MP2/6-31G*//6-31G*	-225.51615
MP3/6-31G*//6-31G*	-225.53111

	a	b	c	d	e	f	g	h	i	j
RHF/STO-3G	1.347	1.411	1.316	1.385	1.391	105.9	111.2	104.3	112.1	106.5
RHF/3-21G	1.353	1.395	1.300	1.368	1.385	105.8	109.7	106.2	111.1	107.1
RHF/6-31G*	1.350	1.372	1.289	1.349	1.372	105.2	110.5	105.3	112.2	106.8
MP2/6-31G*	1.378	1.378	1.326	1.366	1.375	104.9	111.0	104.9	111.6	107.6
Exp.[3]	1.358	1.378	1.326	1.349	1.369	106.3	109.8	105.4	111.3	107.2

Sum of the differences of the calculated and the experimental values for tautomer 1

$(|\Delta a + \Delta b + \Delta c + \Delta d + \Delta e|$ for the bonds and $|\Delta f + \Delta g + \Delta h + \Delta i + \Delta j|)$ for the angles.

Theor. Model	Bond(Å)	Angle(°)
RHF/STO-3G	0.112	3.4
RHF/3-21G	0.083	1.7
RHF/6-31G*	0.053	3.1
MP2/6-31G*	0.043	3.7

Figure 1. Energy and geometry characteristics of the most stable imidazole tautomer.

vectors of the transition structures were carefully examined and visualized by a graphical program. The movements point in the direction of the formation or breaking of the new bond corresponding to the forward and backward reaction, respectively. We have no reason to assume that at the RHF/6-31G* theory level there are other minima along the potential energy surface.

Results and Discussion

Before discussing the transition states and their activation energies we will present our results on the different tautomeric[3] forms of imidazole. Imidazole can exist in three tautomeric forms. One of the advantages of computational methods is that they can calculate the energies of the species that are not experimentally available. We optimized all three tautomeric forms, and the energy and structural characteristics of the most stable tautomer are presented in Figure 1. The highest similarity of the bond lengths to the experimental X-ray structure was obtained with the MP2/6-31G* theoretical model, while the angles do not correlate well with the level of calculation. In fact, the highest agreement in the angles of tautomer 1 with the experimental values was obtained at the RHF/3-21G level. The energies and geometries of the other two isomers are presented in Figure 2.

It is evident that tautomer 1 has the lowest energy. For example, with the highest employed theoretical

model, MP2/6-31G*, tautomer structure 1 is preferred by 14.9 kcal/mol over tautomer 2 and 15.8 kcal/mol over tautomer 3. Prior to consideration of the activation barrier of the cycloaddition of ethylene and oxygen to all three imidazole tautomers 1—3, the qualitative order of imidazole tautomers reactivity will be discussed.

A qualitative view of imidazole reactivity with two very different dienophiles such as ethylene and oxygen can be obtained on the basis of the reactant's HOMO—LUMO[13] energy correlation. These two dienophiles have been chosen because they represent two opposite classes of dienophiles for cycloaddition reactions. Ethylene is a common representative of a classical all-carbon dienophile whose reactivity can be changed by either electron-withdrawing or electron-donating substituents. On the other hand, oxygen has two heteroatoms that usually do not undergo cycloaddition reactions because the formation of the carbon—heteroatom bond is less energetically favored and the occupied nonbonding molecular orbitals of the heterodienophile can have profound influence on the stability on the transition state. In this case, the imidazole nitrogen lone pairs can increase this effect.

The energies of frontier orbitals for the separated reactants were calculated at the RHF/6-31G* level, and the results are presented in Table 1.

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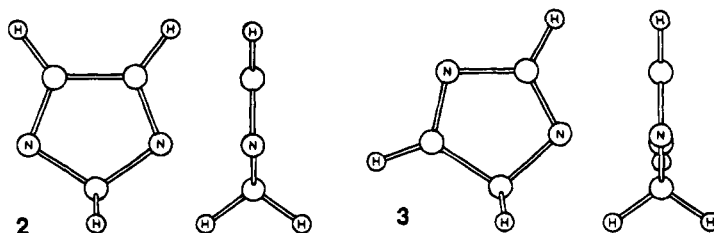
Theor. Model	Total energy/au	Total energy/au
RHF/STO-3G	-221.97668	-221.97576
RHF/3-21G	-223.51268	-223.51244
RHF/6-31G*	-224.79636	-224.79782
MP2/6-31G*	-225.49552	-225.49402
MP2/6-31G*//HF/6-31G*	-225.49088	-225.49031
MP3/6-31G*//HF/6-31G*	-225.51057	-225.51026

Figure 2. Structures and total energies of the two higher energy tautomeric structures of imidazole.

Table 1. Energy (eV) Difference Between the Frontier Orbitals of the Reactants Calculated with RHF/6-31G*

imidazole tautomer	ethylene		oxygen	
	ΔE(FMO1)[a]	ΔE(FMO2)[b]	ΔE(FMO1)	ΔE(FMO2)
1	0.503	0.571	0.370	0.647
2	0.597	0.479	0.463	0.555
3	0.582	0.485	0.448	0.560

[a] ΔE(FMO1) = $LUMO_{dienophile}$−$HOMO_{imidazole}$. [b] ΔE(FMO2) = $LUMO_{imidazole}$−$HOMO_{dienophile}$.

According to FMO theory the pair of reactants with the lowest frontier orbital energy gap is likely to produce the major isomer in the reaction mixture. In the case of ethylene, it was predicted that the reaction is HOMO dienophile controlled and is likely to involve imidazole tautomer **2**. The singlet oxygen is LUMO dienophile controlled addition, and it is predicted to be preferred with imidazole tautomer **1**. Besides, in the oxygen addition the energy difference between the LUMO of oxygen and the HOMO of imidazole tautomer **1** (0.370 eV) is lower than the HOMO of ethylene and the LUMO of imidazole **2** (0.479). On the basis of these data it can be predicted that singlet oxygen should be more reactive than ethylene in the addition to imidazole. Evaluation of the reactivity by FMO has to be taken with caution. First, conclusions can be drawn only for similar systems, and they can be applicable in the comparison of the reactivity of the imidazole tautomers with either oxygen or ethylene, but comparing the two series is highly dubious. Second, this theory studies the reactants separately without incorporating the possible *extra* interactions of the reactants in the transition state. That is especially the case for the oxygen addition to imidazole, because considerable oxygen lone pair and imidazole π-orbital electron repulsion interactions might occur in the course of the reaction.

To eliminate these disadvantages, the reaction barriers of these reactions were calculated and used for the determination of the imidazole tautomer reactivity. According to transition state theory the reaction with the lowest activation barrier is likely to produce the corre-

sponding adduct as a major product.[14] The geometries of the transition states with ethylene and singlet oxygen are presented in Figures 3 and 4, respectively. For the addition of ethylene to tautomer **1** two isomeric transition structures can be envisiged, **4** (Figure 3) and another where the hydrogen is anti to the incoming dienophile. However, the search for the second transiton state was not succesful. In both series concerted, although not always synchronous, transition structures were obtained. That is quite similar to what is known for the all-carbon,[15] as well as some hetero Diels—Alder reactions.[16] The degree of asynchronicity can be determined by comparing the bond distances for the two new forming bonds. However, that can be used only when the two bonds are of the same nature. For example, in case of the adducts going through transition structures **5** and **8** both new forming bonds are of the same nature, i.e., C—C and O—C, while for the rest of transition states the two new forming bonds are of different nature. Fully synchronous transition states were obtained with imidazole tautomer **2** because in the transition states **5** and **8** the reactants are bisected by the plane of symmetry along the reaction pathway. For determining the synchronicity of the other transition structures a better approach is the comparison of the bond orders[17] of the two new forming bonds in the transition states. The bond order calculations were performed at the same level as the calculation of the transition state geometries (Table 2). The highest degree of asynchronicity is predicted for

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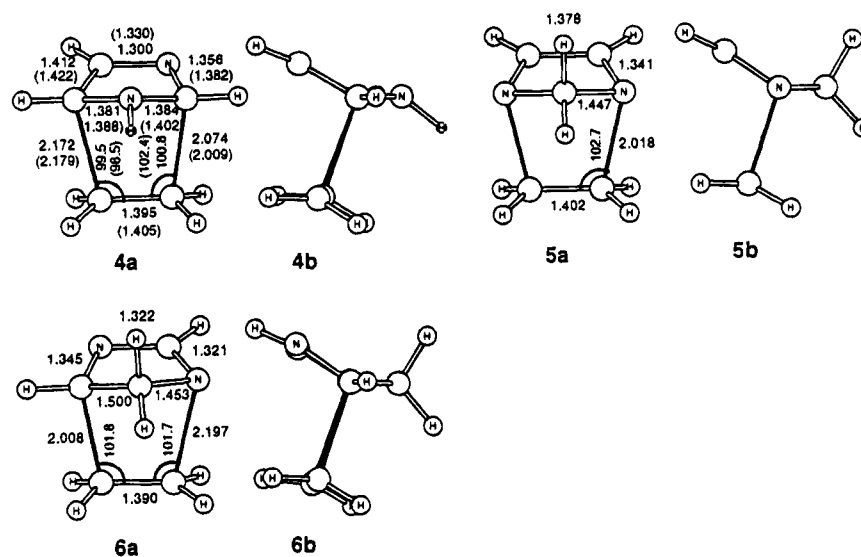
Figure 3. Transition states for the ethylene addition to the three imidazole tautomers generated with RHF/6-31G* and MP2/6-31G* (in brackets).
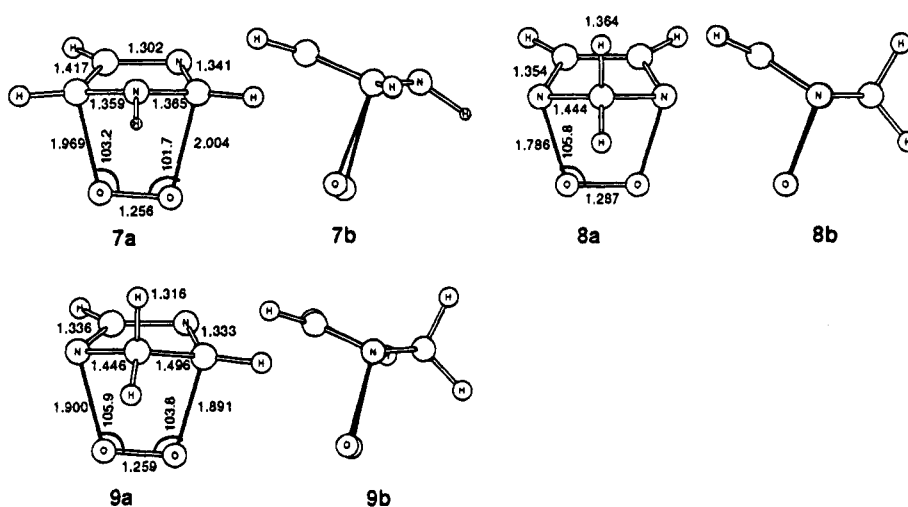

Figure 4. Transition structures of singlet oxygen addition to the three imidazole tautomers generated by RHF/6-31G*.

Table 2. Mulliken Bond Orders[18] of the New Forming Bonds for Singlet Oxygen and Ethylene Addition to Imidazole

TS[a]	RHF/3-21G				RHF/6-31G*			
	a^b	b^c	$|a-b|$	$a+b$	a	b	$|a-b|$	$a+b$
4	0.328	0.358	0.030	0.686	0.323	0.355	0.032	0.678
5	0.293	0.293	0.000	0.586	0.369	0.369	0.000	0.738
6	0.293	0.226	0.067	0.519	0.377	0.268	0.109	0.645
7	0.266	0.265	0.001	0.531	0.399	0.357	0.042	0.756
8	0.354	0.354	0.000	0.708	0.512	0.512	0.000	1.024
9	0.284	0.247	0.037	0.531	0.439	0.364	0.075	0.803

[a] TS, transition structure. *[b]* a, left forming bond of TS presented in Figures 3 and 4. *[c]* b, right forming bond of TS presented in Figures 3 and 4.

Table 3. Total Energies (au) for Transition States Involved in Oxygen and Ethylene Addition to the Imidazole Tautomers

species	$E1^a$	$E2^b$	$E3^c$	$E4^d$
4	−301.083 98	−302.771 02	−303.766 11	−303.787 79
5	−301.039 42	−302.726 82	−303.731 52	−303.749 55
6	−301.057 53	−302.756 53	−303.749 44	−303.771 25
7	−372.230 32	−374.311 47	−375.423 36	−375.411 97
8	−372.154 17	−374.224 67	−375.345 13	−375.333 11
9	−372.175 34	−374.264 59	−375.375 48	−375.364 96

[a] $E1$, RHF/3-21G//RHF/3-21G. *[b]* $E2$, RHF/6-31G*//RHF/6-31G*. *[c]* $E3$, MP2/6-31G*//RHF/6-31G*. *[d]* $E4$, MP3/6-31G*//RHF/6-31G*.

tautomer **3** additions: for the ethylene addition the difference in the bond orders for the new forming bonds is 0.109, and for the singlet oxygen addition it is 0.075 (Table 2). Sometimes the degree of reaction advance can be also used as a qualitative method for determination of the reactivity of similar compounds. In this respect, the earliest transition state, or in other words the one that has advanced the least, should have the lowest energy barrier. In the ethylene addition, tautomer **3**, and in the case of oxygen addition, tautomer **1** (RHF/6-31G*)

is predicted to be the most reactive (Table 2). However, again the comparison of the bond orders between two series is questionable and cannot be used to compare the reactivity of ethylene and singlet oxygen in cycloaddition reactions to imidazole.

As mentioned above the activation energies of the reactions are the most reliable approach to determine the reactivity of the different imidazole tautomers. The total energies and activation barriers for these reactions are presented in Tables 3 and 4, respectively.

The results will be compared with the activation energy

Table 4. Activation Energies (kcal/mol) for Ethylene and Singlet Oxygen Addition to Tautomers of Imidazole

TS	$\Delta E1^a$	$\Delta E2^b$	$\Delta E3^c$	$\Delta E4^d$
4	41.5	47.1	21.6	30.5
5	46.6	63.5	27.4	41.7
6	35.1	45.8	15.8	27.8
7	3.7	22.6	−12.9	0.6
8	28.7	65.7	20.6	37.2
9	15.2	41.6	0.9	17.1
10^e	32.5	40.1	13.0	23.4

^{a} $\Delta E1$, RHF/3-21G. ^{b} $\Delta E2$, RHF/6-31G*. ^{c} $\Delta E3$, MP2/6-31G*// RHF/6-31G*. ^{d} $\Delta E4$, MP3/6-31G*//RHF/6-31G*. ^{e} From ref 20.

for the ethylene addition to butadiene (10) which has been experimentally determined to be 25.1 kcal/mol.[19] This example of the cycloaddition reaction was chosen because both experimental and theoretical data[20] are very well known, as well as the fact that performing the cycloaddition reaction with that reaction barrier requires rather drastic reaction conditions. The calculated activation energy strongly depends on the theoretical model employed. Of all imidazole tautomers, tautomer 3 is the most reactive toward ethylene. That can be explained by the higher energy of tautomer 3 over the others, thus lowering its activation barrier. The highest activation energy was obtained with tautomer 2 because two C−N bonds are formed and the repulsion interactions between the nitrogen lone pair of imidazole and the π-orbitals of ethylene in transition structure 5 are maximal.[16b] Transition state 4, for the ethylene addition to imidazole tautomer 1, was also generated at the MP2/6-31G* level. Although the geometry parameters are quite different than the ones obtained at the HF/6-31G* or HF/3-21G levels, the energy evaluations at MP2/6-31G* are very similar. However, it is well documented that the energies at the MP2 level are underestimated[15a] and only the higher orders of correlation can give more reliable activation energies. The activation energy at the MP3/6-31G*/ /HF/6-31G* level is 30.5 kcal/mol, 7 kcal/mol higher than the corresponding butadiene reaction which in this case is not a significant difference from the one obtained at the MP2 level (Table 4). Therefore, it is reasonable to state that Diels−Alder reaction for ethylene and imidazole is more difficult than for ethylene and butadiene.

The negative value for the activation energy for 7 shows that the MP2/6-31G*//HF/6-31G* energies are also underestimated in the case of the oxygen cycloadditions. Nevertheless, it is apparent that imidazole tautomer 1 has considerably lower activation energy at all applied ab initio levels, while tautomer 2 again has the highest activation energy. That can be explained by the fact that in transition state 8 two new N−O bonds are formed that are usually less preferable than the formation of C−O bonds. The possible repulsion interactions between the oxygen and the nitrogen lone pairs and π-orbitals in transition structure 8 also play a role. This explanation makes the oxygen cycloaddition to imidazole tautomer 3

(transition structure 9, Figure 4) as the second most reactive because only one N−O bond is formed and imidazole tautomer 1 (transition structure 7, Figure 4) as the most reactive with no N−O bonds formed. The predicted activation energies confirm this approach. Furthermore, the predicted activation energy at MP3/6-31G*//RHF/6-31G* is only 0.6 kcal/mol (Table 4) and is far below the 23.4 kcal/mol predicted for the ethylene addition to butadiene. It is reasonable to believe that MP3/6-31G*, calculated energies are sufficient to predict relative reactivity of imidazole tautomers, as well as the feasibility of the reaction. According to these predictions the addition of oxygen to imidazole should be swift, contrary to the ethylene addition to imidazole, and the product from imidazole tautomer 1 should be formed. The theoretical prediction that imidazole tautomer 1 will react with singlet oxygen is experimentally known.[4] The reaction goes smoothly, producing the cyclic peroxide through transition structure 7 that can further react with alcohol producing hydantion derivatives.

Conclusion

The different reactivity of imidazole in the addition of unactivated ethylene and heterodienophiles such as oxygen has been addressed by correlation of the frontier orbital energies and the ab initio calculation of the reaction barriers. FMO theory predicts that the ethylene addition is imidazole LUMO controlled, and the LUMO energy for 1 is 0.0631 eV higher than for butadiene. On the other hand, the addition oxygen is HOMO imidazole controlled and the HOMO energy for 1 is 0.0263 eV lower than for butadiene. That makes the imidazole−oxygen reaction pair more reactive. Different levels of ab initio calculations were applied, and in all cases the oxygen addition is preferred over the ethylene addition to imidazole. The activation energies are compared to the calculated activation energy of ethylene addition to butadiene, and in the case of imidazole the activation energy for ethylene addition is considerably higher. However, the activation energy for the oxygen addition to imidazole is much lower than, for example, in the case of ethylene addition to butadiene. Because the HOMO of imidazole is relatively low and the aromatic stability high, and also since the presence of the lone pair orbital on nitrogen can destabilize the transition structures of the corresponding transition states, this diene will undergo Diels−Alder reactions only with dienophiles that have very high LUMO energy, like oxygen, or very low HOMO energy like dimethoxyethene. The product will be formed with imidazole tautomer 1 because in the corresponding transition state the repulsion interaction between the filled orbital is minimal.

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