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A Semiempirical (AM1, MNDO, and MINDO/3) Study on the Thermolysis of 1-Alkynyl Ethers. Reaction Analysis by Correlation of Localized Molecular Orbitals

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The thermolyses of ethoxyethyne (**2a**), isopropoxyethyne (**2b**), *tert*-butoxyethyne (**2c**), 1-ethoxy-1-propyne (**3a**), 1-isopropoxy-1-propyne (**3b**), 1-*tert*-butoxy-1-propyne (**3c**), and 1-ethoxy-1-butyne (**4**) leading to ketenes and olefins have been studied by means of the semiempirical SCF MO methods AM1, MNDO, and MINDO/3 at the RHF level. The reactions have been found in all cases to be concerted and to exhibit a highly synchronous character. The predicted order of reactivity, $-C{\equiv}CO\text{-}t\text{-}Bu > -C{\equiv}CO\text{-}i\text{-}Pr > -C{\equiv}COEt$, fully coincides with the experimental one, the AM1 calculated activation enthalpies being the closest to the experimentally determined Arrhenius activation energies. Observed deuterium primary and secondary kinetic isotope effects are well reproduced by the calculation. A reaction analysis by correlation of localized molecular orbitals identifies the direction of flow of electron density along the reaction coordinate and suggests that the lack of adaptation of the σ-component of the initial triple bond to the geometrical changes taking place along the reaction path makes an important contribution to the activation energy of the reaction.

Introduction

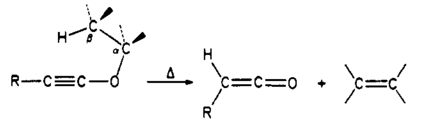
1-Alkynyl ethers bearing hydrogen atoms β to oxygen are thermally unstable, readily fragmenting into an olefin and a ketene at moderate temperatures[1] (Scheme I). The ease of the fragmentation is roughly proportional to the number of β-hydrogen atoms. Thus, 1-ethoxy-1-alkynes lose ethylene when heated at 120 °C, while 1-*tert*-butoxy-1-alkynes split off into 2-methylpropene and a ketene below 80 °C.

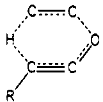
This process, first described by Ficini[2] in 1954, was extensively studied by the Arens group in the subsequent years both from the synthetic and from the mechanistic points of view.[3-5]

The main synthetic features of this reaction are the preparation in high yield of cyclobutenone ethers,[4,6,7] through a 2 + 2 cycloaddition between the generated ketene and the starting 1-alkynyl ether, the stereospecific generation of olefins with complete absence of isomerization (when the reaction is performed in the presence of a ketene trap such as aniline[5]), and the generation of ketenes not prone to undergo 2 + 2 cycloaddition reactions, such as (trimethylsilyl)ketene[8] and ketene itself.[9]

From the mechanistic point of view, Olsman[5] has shown that the thermolysis of 1-alkynyl ethers is first order and essentially homogeneous, the rate constants being not affected by the presence of radical scavengers; it has a negative entropy of activation and shows significant primary and secondary deuterium kinetic isotope effects. Alkyl substituents on the acetylenic carbon slightly accelerate the reaction, and a stronger acceleration is provoked by branching α to oxygen in the alkoxy group. This acceleration is due in part to statistical factors (i.e., to the greater number of β-hydrogen atoms available for reaction) and in part to electronic factors, as reflected by a decrease in E_a (see below). All these facts are consistent with a concerted mechanism proceeding through the six-center transition state represented by **1**.[10]

Scheme I





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Up to now, no theoretical study has been devoted to the thermolysis of 1-alkynyl ethers. Due to our fundamental interest in the various aspects of this reaction, we decided to perform a comprehensive examination of the thermolysis of a family of such compounds, namely, **2a–c**, **3a–c**, and **4**, in order to get a theoretically based confirmation of the concerted nature of the reaction, to study the effect of both the nature of the alkoxy group (primary, secondary, or tertiary) and the substitution by alkyl groups at the other acetylenic carbon on the calculated activation parameters, and to try to reproduce the experimentally reported deuterium kinetic isotope effects.

$$\underset{\textbf{2a–c}}{HC{\equiv}COR}\quad \underset{\textbf{3a–c}}{CH_3C{\equiv}COR}\quad \underset{\textbf{4}}{CH_3CH_2C{\equiv}COCH_2CH_3}$$

a, R = CH_2CH_3; **b**, R = $CH(CH_3)_2$; **c**, R = $C(CH_3)_3$

The size of the molecular systems involved in our study precluded the use of ab initio methodology and strongly recommended the use of a semiempirical, yet reliable, SCF MO method. MINDO/3,[11] MNDO,[12] and AM1,[13] the

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Table I. Relevant Geometrical Parameters[a,b] in the AM1, (MNDO), and [MINDO/3] Optimized Transition States for the Thermolysis of 1-Alkynyl Ethers 2a-c, 3a-c and 4

compd	r_{12}	r_{23}	r_{34}	r_{45}	r_{56}	r_{61}
2a	1.258	1.245	1.896	1.409	1.352	1.423
	(1.290)	(1.258)	(1.566)	(1.443)	(1.709)	(1.207)
	[1.303]	[1.228]	[1.529]	[1.393]	[1.746]	[1.181]
2b	1.253	1.243	1.974	1.417	1.308	1.485
	(1.289)	(1.254)	(1.596)	(1.449)	(1.674)	(1.216)
	[1.302]	[1.225]	[1.564]	[1.406]	[1.710]	[1.186]
2c	1.249	1.242	2.051	1.426	1.276	1.541
	(1.287)	(1.249)	(1.642)	(1.456)	(1.622)	(1.231)
	[1.301]	[1.223]	[1.604]	[1.422]	[1.667]	[1.192]
3a	1.262	1.243	1.915	1.407	1.348	1.434
	(1.295)	(1.252)	(1.584)	(1.438)	(1.708)	(1.216)
	[1.315]	[1.224]	[1.537]	[1.390]	[1.763]	[1.196]
3b	1.257	1.241	1.994	1.416	1.305	1.494
	(1.294)	(1.247)	(1.625)	(1.443)	(1.659)	(1.229)
	[1.314]	[1.221]	[1.574]	[1.403]	[1.725]	[1.201]
3c	1.252	1.240	2.071	1.424	1.274	1.549
	(1.287)	(1.237)	(1.744)	(1.447)	(1.531)	(1.278)
	[1.313]	[1.219]	[1.617]	[1.418]	[1.680]	[1.208]
4	1.262	1.243	1.914	1.407	1.346	1.434

[a] Atom numbering as defined in Figure 1. [b] r_{xy} are the distances in angstroms between atoms x and y.

Table II. AM1, (MNDO), and [MINDO/3] Calculated Thermochemical and Activation Parameters[a,b] for the Thermolysis of 1-Alkynyl Ethers 2a-c, 3a-c, and 4

compd	ΔH_r	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
2a	-7.0	46.3	-4.4
	(-5.9)	(76.6)	(-5.2)
	[4.7]	[52.9]	[-8.8]
2b	-12.2	43.7	-3.1
	(-14.5)	(75.0)	(-4.0)
	[-6.0]	[47.4]	[-7.9]
2c	-17.9	40.5	-2.3
	(-22.9)	(73.7)	(-3.3)
	[-12.9]	[45.9]	[-7.9]
3a	-4.4	46.6	-7.7
	(-0.0)	(80.4)	(-6.7)
	[13.6]	[58.3]	[-8.8]
3b	-9.6	43.8	-6.7
	(-9.1)	(78.1)	(-5.2)
	[2.8]	[52.6]	[-7.7]
3c	-15.2	40.5	-6.7
	(-17.5)	(76.5)	(+3.8)
	[-4.0]	[51.1]	[-7.4]
4	-6.0	46.8	-4.9

[a] Enthalpies of reaction (ΔH_r) and enthalpies of activation ($\Delta H^{\ddagger}$) are at 298 K in kcal mol^{-1}. [b] Activation entropies ($\Delta S^{\ddagger}$) are at 298 K in cal mol^{-1} deg^{-1}.

semiempirical procedures developed by Dewar and coworkers, were selected for the following reasons: (i) Both MINDO/3 and MNDO are well-established procedures for the study of chemical reactions, and MINDO/3 has proved to perform well in the description of a similar unimolecular process, such as the retro-ene decarboxylation of but-3-enoic acid,[14] and (ii) the alleged tendency of MINDO/3 and MNDO to give an stepwise description of chemical reactions and to overestimate reaction barriers appears to have been solved, at least in part, in the AM1 treatment. On the other hand, there has been some controversy on the ability of ab initio or semiempirical SCF MO method to describe the transition states of pericyclic reactions which are allowed in the Woodward–Hoffmann sense. The reaction analyzed in the present study, which falls into this category, appears as an excellent test for the study of the relative merits and defficiencies of the MINDO/3, MNDO, and AM1 procedures in a case where a comparison with a considerable body of experimental data can be made.

Theoretical Procedure

All calculations reported in the present paper were performed with the standard versions of MINDO/3, MNDO, and AM1, as implemented in a locally modified version of the MOPAC package of programs[15] which includes the AM1 parameters. The RHF version was used throughout the study after testing and eliminating the existence of diradical character in all transition states by means of single-point UHF calculations. Geometries for stationary points were determined by minimization of the energy with respect to all geometrical parameters using the DFP algorithm.[16] Transition states (TS) were located either by the normal reaction coordinate method or with the NLLSQ algorithm,[17] refined by minimizing the gradient norm of the energy,[18] and characterized by establishing that the Hessian (force constants) matrix had one, and only one, negative eigenvalue.[18] Entropies of activation were calculated with the standard THERMO option in MOPAC. As a complementary criterion, the progress of the reactions was followed by means of the bond index B(A–B) between atoms A and B, as defined by eq 1, where

$$B(\text{A–B}) = \sum_{\gamma}\sum_{\sigma} P_{\gamma\sigma}^{2} \qquad (1)$$

$P_{\gamma\sigma}$ values are the elements of the density matrix, and where the subscripts γ and σ refer to atomic orbitals centered at atoms A and B, respectively.

On the other hand, in order to get a deeper insight on the electronic reorganization taking place during the reaction, the localized molecular orbitals (LMOs) of the reactants, products and transition states were calculated by means of the localization procedure implemented in MOPAC, which essentially consists in a reformulation[19] of the Von Niessen density–localization criterion.[20] As

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Table III. Evolution of Relevant Bond Indices[a] along the Reaction Coordinate for the Thermolysis of 1-Ethoxyethyne According to AM1, (MNDO) and [MINDO/3]

reactn stage	B_{12}	B_{23}	B_{34}	B_{45}	B_{56}	B_{61}
ethoxyethyne	2.810	1.091	0.926	0.991	0.971	0.001
	(2.815)	(1.082)	(0.927)	(0.964)	(0.976)	(0.000)
	[2.730]	[1.025]	[0.903]	[0.967]	[0.959]	[0.002]
transition state	2.157	1.545	0.392	1.386	0.502	0.360
	(1.977)	(1.433)	(0.599)	(1.309)	(0.268)	(0.671)
	[1.844]	[1.417]	[0.453]	[1.459]	[0.203]	[0.696]
ketene + ethylene	1.748	2.015		2.002		0.921
	(1.719)	(2.053)		(1.986)		(0.947)
	[1.670]	[1.876]		[1.990]		[0.923]
% bond index in TS	−61.5	+49.1	−57.7	+39.1	−48.3	+39.0
	(−76.5)	(+36.1)	(−35.4)	(+33.8)	(−72.5)	(+70.9)
	[−83.6]	[+46.1]	[−49.8]	[+48.1]	[−78.8]	[+75.4]

[a] Atom numbering, as defined in Figure 1 for the transition state, is retained for starting material and products.

it will be seen later, this localization procedure usually leads to σ–π separated LMOs,[19a] contrary to what is commonly observed when the Boys method[21] is used.

Results and Discussion

Table I summarizes the relevant geometrical parameters of the transition states in the thermolysis of **2a–c**, **3a–c**, and **4**, and the thermochemical and activation parameters for the thermolysis reactions are summarized in Table II.

The first important point to be noted is that, in all the studied cases, the reactions are predicted to be concerted and highly synchronous by either of the three different semiempirical methods used. In the AM1 transition states the transferring hydrogen atom is half-way between C_5 and C_1 (compare r_{56} and r_{61}), whereas the cleavage of the O_3–C_4 bond is already in a more advanced stage. By the contrary, both MNDO and MINDO/3 give TS's where the hydrogen atom has already been essentially transferred from C_5 to C_1, but where the O_3–C_4 bond is still important. Figure 1 shows the AM1 and MINDO/3 calculated transition structures for the thermolysis of ethoxyethyne, where the forementioned differences can be properly appreciated, along with the corresponding AM1 calculated TS's for the thermolyses of isopropoxyethyne **2b** and *tert*-butoxyethyne **2c**.

The effect on the transition states of branching by alkyl groups α to oxygen in the alkoxy moiety is that of increasing the extent of the O_3–C_4 bond cleavage, while retarding the transfer of H_6 from C_5 to C_1. The nonsynchronicity of the process is, therefore, enhanced. A parallel effect, though much weaker, is provoked by alkyl substitution on the acetylenic carbon. These findings are consistent with the intuitive idea that the nature of the alkene to be formed in the elimination process will importantly influence the course of the reaction. Thus, the greater ability of alkyl-substituted carbons for stabilizing a partial positive charge can be responsible for the increased cleavage of the O_3–C_4 bond when the branching of the alkoxy group increases. In this sense, it is worth noting that the charge developed on the C_4 atom in the transition states uniformly increases from −0.0393 in **2a** to +0.1147 in **2c**. Another point that deserves comment is the almost strictly planar arrangement of the six centers directly implied in the reaction in the transition states.

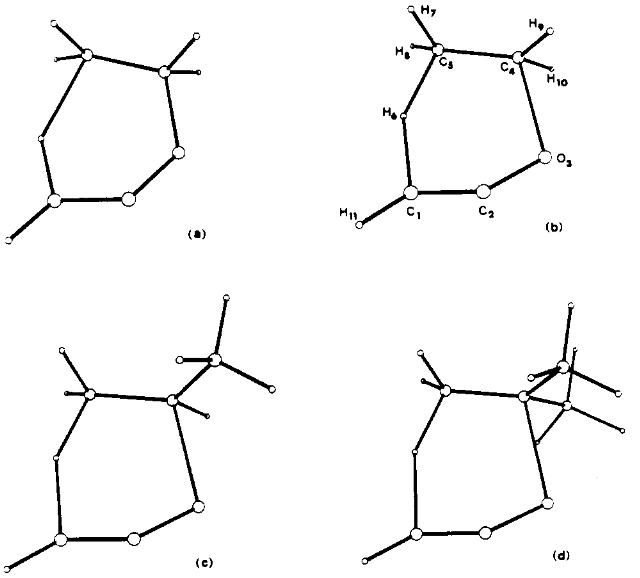

Figure 1. Computer plot of the calculated transition states for the thermolyses of (a) ethoxyethyne (MINDO/3), (b) ethoxyethyne (AM1), (c) isopropoxyethyne (AM1), and (d) *tert*-butoxyethyne (AM1).

The bond index criterion affords a complementary vision of the thermolysis process. Table III shows, as an example, the evolution along the reaction path of the bond indices corresponding to the bonds which are made or broken in the thermolysis of ethoxyethyne. Relevant bond indices of the transition states for the thermolysis of 1-alkynyl ethers **2a–c**, **3a–c**, and **4** are given in the supplementary material. As it can be seen, AM1 describes the reaction as taking place with a high degree of synchronicity, all the bond-breaking and all the bond-forming processes having proceeded at a comparable extent (40–60%) in the transition state. Even the long O_3–C_4 bond (1.896 Å) retains a 42% of its initial index. On the other hand, both MNDO and MINDO/3 make a more asynchronous description of the reaction, the π component of the initial triple bond involved in the reaction and the C_5–H_6 bond being both importantly broken in the transition state, whereas the C_1–H_6 bond has already formed at a very considerable extent. This is in accord with the expected outcome of AM1 when compared with MINDO/3 and MNDO. The general trends observed for the thermolysis of ethoxyethyne are reproduced in the thermolysis of the other 1-alkoxyalkynes subject of the present study. As a final comment on the character of the thermolysis of 1-alkynyl ethers, it should be emphasized that this is one of the very few examples of reactions predicted to be not only concerted but also notably synchronous by MINDO/3, MNDO, and AM1. As Dewar has pointed out,[22] multibond reactions that involve migration of a hydrogen atom tend

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Table IV. Experimentally Determined Activation Parameters[a,b] for the Thermolysis of Some 1-Alkynyl Ethers

compd	E_a	$\Delta S^{\ddagger}$
$CH_3CH_2C{\equiv}COC(CH_3)_3$	23	−15
$CH_3CH_2C{\equiv}COCH(CH_3)_2$	26	−10
$CH_3CH_2C{\equiv}CO(CH_2)_3CH_3$	29	−6
$CH_3(CH_2)_4C{\equiv}COCH_2CH_3$	29	−12

[a] Values measured in solution of decalin at 358–388 K (ref 5). [b] E_a in kcal mol^{-1} and $\Delta S^{\ddagger}$ in cal mol^{-1} deg^{-1}.

to be synchronous as a consequence of the high strength of two-electron three-center bonds involving hydrogen. The thermolysis process studied here clearly fits into this category.

Thermochemical and Activation Parameters. No heats of formation of 1-alkynyl ethers allowing the determination of enthalpies of reaction for the thermolysis process have been reported in the literature nor a direct measure of the enthalpy of reaction for the pure thermolysis of 1-alkynyl ethers can likely be performed since the thermolysis step cannot be in general separated from a subsequent 2 + 2 cycloaddition reaction between the generated ketene and the starting 1-alkynyl ether. The 2 + 2 cycloaddition is assumed to be much faster than the thermolysis, and a recent theoretical study by the MNDO method on the model 2 + 2 cycloaddition of dihydroxyethyne with hydroxyketene[23] tends to confirm this assumption in view of the results of the present study.

From the theoretical point of view (Table II), all three semiempirical methods used in the present study predict that, within a given family of 1-alkynyl ethers (i.e., **2** or **3**), the reactions become more exothermic as the branching of the alkoxy group increases. This evolution mainly reflects the greater stability of the alkyl-substituted ethylenes arising from the reaction relative to the parent ethylene, as indicated by the fact that, within a given methodology and for a given family of 1-ethynyl ethers of the same type (**2** or **3**), the difference in ΔH_r approaches the difference in calculated heats of formation[11–13] between the alkenes that would be formed in the pyrolysis.

On the other hand, the introduction of a methyl group on the acetylenic carbon makes the reactions less exothermic by an essentially constant term within a given methodology. This is equivalent to say that the isodesmic reaction shown in eq 2 is exothermic by the same term,

$$CH_3CH{=}C{=}O + HC{\equiv}COR \rightarrow H_2C{=}C{=}O + CH_3C{\equiv}COR \quad (2)$$

which ultimately reflects the differential stabilization of a ketene and an ethynyl ether by a methyl group.

The activation parameters for the thermolysis of a family of 1-alkynyl ethers have been reported by Olsman.[5] Some representative examples are listed in Table IV.

Some general trends can be observed in these values. In the first place, the introduction of an alkyl substituent α to oxygen in the alkoxy group uniformly provokes a decrease of 3 kcal mol^{-1} in E_a. On the other hand, the activation entropies are strongly negative and consequently indicative of a highly ordered transition state.

In comparing the calculated activation parameters (Table II) with the experimental ones, it first appears that all three semiempirical procedures give an ordering of $\Delta H^{\ddagger}$ according with the experimental one, a decrease in $\Delta H^{\ddagger}$ being observed as the branching of the alkoxy group increases. However, the MNDO values are completely unrealistic. This fact can probably be attributed to the known tendency of MNDO to overestimate repulsive interactions between atoms when the distance between them is 1.5–2.0 times the length of a corresponding covalent bond.[22] As it can be seen in Table I, r_{56} lies in this region. Noteworthy, MINDO/3 gives a proper description of the activation enthalpies. In any case, the AM1 calculated activation enthalpies are the closest to the experimental values, the observed decrease in 3 kcal mol^{-1} in the activation energy per additional methyl group α to oxygen being perfectly reproduced by the calculations. Even so, the calculated values are uniformly greater by 17 kcal mol^{-1} than the corresponding experimental ones. It is worth noting that Dewar and co-workers have found an identical difference between the experimental and calculated energies of activation for the degenerate 1,5-hydrogen shift in malonaldehyde enol.[13]

Table V. Calculated and (Experimental)[a] Primary (k_{H3}/k_{D3}) and Secondary (k_{D3}/k_{D5}) Deuterium Kinetic Isotope Effects in the Thermolysis of some 1-Ethoxy-1-alkynes

compd	k_{H3}/k_{D3}	k_{D3}/k_{D5}
2a	3.007	1.147
3a	2.995	1.158
4	2.990 (3.4)	1.157 (1.15)

[a] Measured at 381.8 K in decalin solution (ref 5).

In summary, AM1 appears to give the most accurate description of the activation enthalpies for the thermolysis of 1-alkynyl ethers; not only is the experimental order of reactivity well reproduced but also the difference between the activation energies for the thermolysis of individual compounds are quantitatively predicted in a correct way. Keeping this fact in mind, we will restrict ourselves to AM1 results for the discussions in the next sections.

Kinetic Isotope Effects. Olsman[5] studied the existence of deuterium kinetic isotope effects in the thermolysis of 1-alkynyl ethers. Working with 1-(2,2,2-trideuterioethoxy)-1-butyne, he found a *primary* isotopic effect (k_{H3}/k_{D3}) of 3.4. In order to obtain information on the secondary isotopic effect, he also performed the thermolysis of 1-(pentadeuterioethoxy)-1-butyne, finding that $k_{D3}/k_{D5} = 1.15$. The experiments were performed at 381.8 K, where the theoretical maximum primary isotopic effect is 4.4. These results were consequently interpreted as indicative of a transition state with a nearly half-transferred β-hydrogen atom. Our present theoretical findings fully confirm this interpretation (see the AM1 results for **2a**, **3a**, and **4** in Table I).

Since the MOPAC package of programs offers an advantageous alternative for the calculation of vibrational frequencies of isotopically labeled species starting from the force constant (Hessian) matrix of the nonlabeled species, it appeared as interesting to calculate the *primary* and *secondary* deuterium kinetic isotope effects (as defined by Olsman) in a series of 1-ethoxy-1-alkynes. The calculations were performed according to the commonly used Biegeleisen and Goeppert-Mayer equation.[24] The results are given in Table V along with the experimental values where available.

Quite interestingly, a very good agreement between calculated and experimental values is observed. Since the theoretical procedure used is strictly valid only for the rigid-rotor-harmonic-oscillator case, it could be thought that the small differences observed between the experimental and calculated primary isotopic effect can be due

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to nonrigidity. However, the fact that the calculated secondary isotopic effect has a coincident value with the experimental one tends to indicate that the errors due to nonrigidity cancel. Much probably, the experimentally determined "primary" kinetic isotope effect is overestimated due to differential tunneling of hydrogen and deuterium.[25]

Localized Molecular Orbital Correlation Analysis of the Thermolysis of 1-Alkynyl Ethers. Since the publication of the Woodward–Hoffmann rules,[26] it has been customary to follow the evolution of the electronic distribution from reactants to products in an elementary reaction by inspection of the changes experienced by the canonical molecular orbitals (CMOs) along the reaction coordinate. The application of this approach to relatively large molecular systems of low symmetry becomes, however, very difficult, since the symmetry labels of the orbitals, which together with the noncrossing rule are the only guides to assist in the correlation of CMOs, are then of little (if any) utility. As Trindle and Sinanoglu pointed out several years ago,[27] these difficulties can be circumvented by the use of localized molecular orbitals (LMOs). The high degree of transferability of localized orbitals, which are not adapted to the global symmetry of the molecule and are essentially dependent on the local symmetry of the bond or atom upon which they are centered, makes the correspondence of individual orbitals much more easy to discern, since a given bond orbital or lone pair in the reactants usually corresponds to a similar one in the products. Furthermore, the LMOs corresponding to the bonds which are "made" or "broken" in the reaction usually appear in the transition state in the form of "locally delocalized" orbitals which extend upon the atoms being "joined" or "disconnected" in the reaction. In this way, the LMO correlation from reactants to products through the transition state allows a description of the reaction on terms of the "movement" of bond orbitals and/or lone pairs, directly related to the "curled arrow" picture usually employed by organic chemists in the framework of resonance theory.

Notwithstanding, this approach has been followed only in a limited number of instances. The centroids of charge of LMOs, as determined by the Boys localization method,[21] have been used to follow the electronic change in reactions such as the Diels–Alder reaction,[28] 1–3 dipolar cycloadditions (ethylene + diazomethane,[29] ethylene + ozone,[30] ehtylene + carbonyl ylide[31]), the azido-tetrazole isomerization,[32] and, more recently, the 2 + 2 cycloaddition between ketene and ethylene.[33] The energy-localized orbitals of Edmiston and Ruedenberg[34] have been used in the study of some carbocation rearrangements.[27] In these studies, however, no attention has been paid to the evolution of the LMOs energies along the reaction coordinate, and only in a recent theoretical paper on the concerted dihydrogen exchange between ethane and ethylene the origin of the reaction barrier has been analyzed on the basis of LMOs energies.[35]

The concerted elimination of olefin from 1-ethynyl ethers, subject of the present study, offers a good oportunity for showing the advantages of the LMO correlation approach for the description of theoretical calculations of reaction paths to the non-theoretically oriented organic chemist. As a characteristic example, we will discuss in detail the application of the LMO correlation analysis to the thermolysis of ethoxyethyne within the AM1 approach. The features and conclusions of this analysis apply also for the remainder of 1-ethynyl ethers studied here.

The LMOs of reactant, transition state, and products for the thermolysis of **2a** were obtained with the localization program implemented in MOPAC.[15] It is worth noting that the localization criterion has been chosen in such a way that in the case of multiple bonds and/or lone pairs it will lead in most instances to σ–π separation, so that the correlation analysis is simplified relative to the "banana" bonds produced by the Boys localization criterion.[19a,36]

The local symmetry (i.e., the local σ or π character), orbital energies (i.e., the diagonal elements of the Fock matrix on the LMO basis) and the correlation of the LMOs thus obtained are shown diagramatically in Figure 2. A detailed description of the LMOs can be found in the supplementary material. It is interesting to note that although the sum of twice the orbital energies is by no means equal to the electronic energy of the system (except in the case of the simple Hückel approximation), this quantity is approximately equal to three-halves of the total (nuclear plus electronic) molecular energy,[37] so that the LMOs energies shown in Figure 2 represent in an approximate way the contribution of each bond orbital and lone pair to the energy of the system.

Several points of interest emerge from an inspection of the LMOs. In the first place, it can be seen that in the transition state the σ-bond orbital C_5–H_6 of ethoxyethyne becomes a three-centered orbital with a significant contribution of C_4; in the same way, the σ-bond orbital between C_4 and O_3 becomes a delocalized orbital which embraces C_4, O_3, and C_2, and the π_y-bond orbital C_2–C_1 becomes a three-centered orbital C_2–C_1–H_6. The electronic reorganization during the reaction can thus be represented in terms of electron-pair movement in the way shown in Figure 3. The reaction could be described in the organic chemistry language as a nucleophilic attack of a π-component of the C_1–C_2 triple bond to H_6; the electronic defficiency created in C_2 is simultaneously compensated by the formation of a π-bond between C_2 and O_3, which is accompanied by the formation of the C_5–C_4 π-bond.

The LMO representation of the transition state is thus completely equivalent to that obtained from the bond indices, in that it corresponds to a concerted and almost completely synchronous reaction which involves the pericyclic rearrangement of three two-electron bonds.

Although the physical meaning of the individual orbital energies associated to the LMOs is less clear than in the case of CMOs (whose orbital energies can be related to vertical ionization energies by means of Koopmans' theorem), the changes experienced by the LMOs energies along the reaction coordinate are easily interpretable on the basis of the relationship between bond energy and the hybridization of the corresponding AO components. In fact, an

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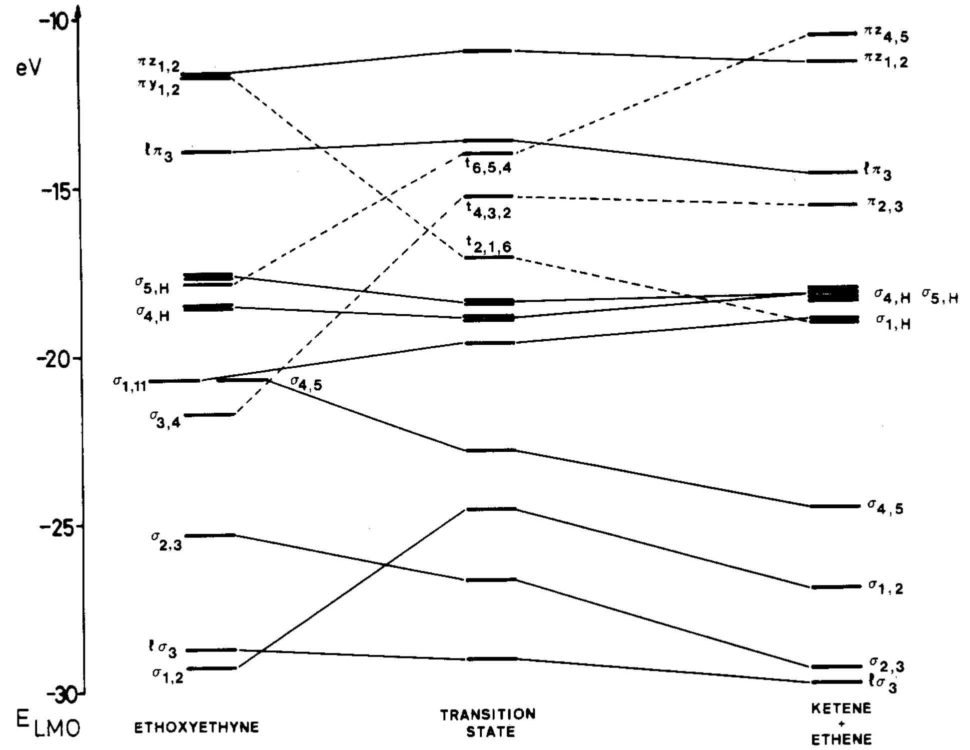

Figure 2. Correlation diagram of the localized molecular orbitals in the thermolysis of ethoxyethyne. Atom numbering, as defined in Figure 1 for the transition state, is retained for starting material and products. The meaning of the labels is as follows: σ and π refer to the local symmetry of localized bicentric orbitals; l_σ and l_π refer to localized monocentric orbitals; t refers to localized tricentric orbitals. The broken lines connect the orbitals corresponding to the bonds which are made or broken in the reaction.

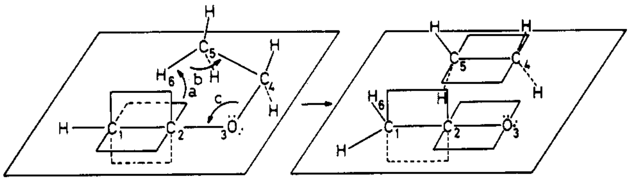

Figure 3. Schematic representation of the electronic reorganization along the reaction path in the thermolysis of ethoxyethyne: (a) $\pi_y(1,2) \rightarrow \sigma(1,6)$; (b) $\sigma(5,6) \rightarrow \pi_y(5,4)$; (c) $\sigma(3,4) \rightarrow \pi_y(2,3)$.

inspection of Figure 2 reveals that, with respect to the orbital energies, the LMOs of the transition state can be classified in three types:

(a) Orbitals whose energy is intermediate between the energies of the corresponding orbitals in reactant and products. These orbitals smoothly adapt themselves to the geometry and hybridization changes experienced by the atoms along the reaction coordinate and should not contribute significantly either to the stabilization or the destabilization of the transition state.

(b) Orbitals whose energy is lower than both the energies of the corresponding orbitals in reactant and products. The role of these orbitals is thus the stabilization of the transition state. This is the case of the two σ-bond orbitals between C_4 and both H_9 and H_{10}. These orbitals have slightly increased their contribution from C_4 with respect to both reactant and products, so that this stabilizing effect can be ascribed to a positive hyperconjugation of these bonds which helps to diminish the electronic defficiency created at C_4 in the transition state.

(c) Orbitals whose energy is higher than both the energies of the corresponding orbitals in reactant and products. The destabilization of the transition state can be thus ascribed to these orbitals. In the present case, this happens to the π_z- and σ-bonds between C_1 and C_2, to the π_z-lone pair centered at O_3, and to the three-center orbital which represents the σ-bond breaking between C_4 and O_3 and the making of the π_y-bond between O_3 and C_2. The main destabilizing effect corresponds to the σ-bond between C_1 and C_2, so that we will now analyze this point in some detail.

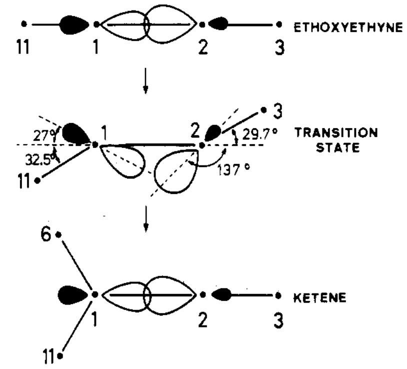

Figure 4. Evolution of the $\sigma(1,2)$ bond orbital along the reaction path in the thermolysis of ethoxyethyne.

In Figure 4 we represent in a schematic and qualitative way the evolution of the $\sigma(C_1{-}C_2)$ bond orbital along the reaction coordinate.

The destabilization in the transition state of this orbital, which corresponds to a bond which is neither made nor broken in the reaction, can be ascribed to two main factors:

(i) In the reactant ethoxyethyne, the $\sigma(C_1{-}C_2)$ bond orbital can be described as the bonding combination of an $sp^{1.04}$ hybrid from C_1 and an $sp^{0.41}$ hybrid from C_2. In the transition state, the C_1 hybrid becomes an $sp^{3.02}$ one, while the C_2 hybridization remains almost the same ($sp^{0.40}$). In the reaction product (ketene), the $\sigma(C_1{-}C_2)$ bond orbital stems from the interaction between a C_1 $sp^{1.97}$ hybrid and a C_2 $sp^{0.46}$ hybrid. The percentage of p character in this bond orbital in the transition state is greater than in reactant or product, so that the energy is accordingly greater.

(ii) As it can be readily seen in Figure 4, the maximum overlap in the $\sigma(C_1–C_2)$ bond orbital in the transition state occurs out of the internuclear axis, and that constitutes another important destabilization factor. This is due to the fact that C_2 is forced to maintain an average sp hybridization along the reaction coordinate, while the transition state geometry imposes a $C_1–C_2–O_3$ angle of 150.3°. The $sp^{0.40}$ hybrid orbital at C_2 is then forced out of the $C_1–C_2$ internuclear straight line in order to maintain a bonding direction approximately opposite to that of the $sp^{1.41}$ component of C_2 in the $\sigma(C_2–O_3)$ bond orbital. In conclusion, the visualization of an elementary reaction in terms of LMOs results in a new way of looking at chemical reactions (provided that the wavefunction remains monodeterminantal along the reaction path[38]), which could be summarized as follows: any elementary chemical reaction involves a geometrical rearrangement of the nuclei along the reaction coordinate, together with a relocation and/or rehybridization of the LMOs (which represent the "classical" electron pairs) of the system. A substantial part of the energetic barrier associated to the transition state could then be due to the fact that *at least one electron pair*, which will be always presumably a bonding one, *is not able to follow adequately the movement of the nuclei*, so that it is not possible for the transition state to maintain a bonding situation comparable to that of reactants and products. An important point that arises from the present study is that *the bonds which are mainly responsible for the energetic destabilization of the transition state are not necessarily those which are made or broken during the reaction*, contrary to what is implied or stated in elementary textbooks; in the present case, the bond orbital which is the most destabilized in the transition state is the σ-component of the acetylenic $C_1–C_2$ triple bond, which does not "intervene" essentially in the reaction since it ends up in the products also as a σ-component of a multiple bond between the same atoms (i.e., the σ-component of the $C_1–C_2$ double bond of ketene). It would be interesting to know if this fact is more general and work along these lines is currently in progress in our laboratory.

Acknowledgment. The calculations were performed with the IBM 3083 computer at the "Centre d'Informàtica de la Universitat de Barcelona". Financial support from the CAICYT (Grant 3218/83) is gratefully acknowledged. We also thank Dr. Juan C. Paniagua and Dr. Santiago Olivella for helpful discussions.

Registry No. **2a**, 927-80-0; **2b**, 36678-59-8; **2c**, 89489-28-1; **3a**, 14273-06-4; **3b**, 89489-29-2; **3c**, 89896-71-9; 4, 14272-91-4; D_2, 7782-39-0.

Supplementary Material Available: Cartesian coordinates of the optimized molecular structures and relevant bond indices in the optimized TS's at the MINDO/3, MNDO, and AM1 levels and the AM1 LMOs for reactant, transition state, and products in the concerted elimination of ethylene from ethoxyethyne (36 pages). Ordering information is given on any current masthead page.

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Dipolar Cycloaddition Reactions of Diazoazoles with Electron-Rich and with Strained Unsaturated Compounds

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Regiospecific net 1,7-cycloaddition reactions of electron-rich or strained olefins and electron-donor acetylenes occur readily (−70 to −10 °C) with diazoazoles having nitrogen in the 2-positions of their azole rings. Diazoazoles such as 5-*tert*-butyl-3-diazo-3*H*-pyrazole (**20**), 3-diazo-5-phenyl-3*H*-pyrazole (**24**), 2-diazo-2*H*-imidazole (**28**), 4,5-dicyano-2-diazo-2*H*-imidazole (**12**), 4-diazo-4*H*-imidazole (**63**), 4-diazo-5-phenyl-4*H*-1,2,3-triazole (**70**), 5-cyano-4-diazo-4*H*-1,2,3-triazole (**74**), 3-diazo-3*H*-1,2,4-triazole (**76**), and 3-diazo-5-phenyl-3*H*-1,2,4-triazole (**79**) thus usually add effectively to unsaturated reactants such as enamines, 1-alkoxyalkenes, ketene acetals, aryl isocyanates, norbornene, and norbornadiene to give new 1,7-cycloadducts. These cyclization reactions may be followed by tautomerization processes leading to new stabilized fused heterocycles or by elimination to novel highly delocalized heteroaromatic derivatives. 4,5-Dicyano-2-diazo-2*H*-imidazole (**12**) undergoes various accelerated cycloadditions to unsaturates and adds to norbornene and norbornadiene by exclusive exo dipolar proceses. Addition of activated acetylenes to representative α-diazoazoles also results in regiospecific 1,7-cyclization to give stabilized fused azolo heterocycles.

Regiospecific 1,7-cycloaddition reactions (eq 1 and 2) of 3-diazo-3*H*-pyrazoles (**1**, X = N, Y and Z = C–R), 4-diazo-4*H*-1,2,3-triazoles (**1**, X and Y = N, Z = C–R), and related diazoazoles with electron-rich olefins and acetylenes were discovered in this laboratory[1] and by Ege[2] and by Dürr[3] and their colleagues. Such additions were theorized to occur directly by thermally allowed (4*n* + 2 electron) 1,7-cyclic processes and/or by allowed (4*n* + 2 electron) 1,3-cyclizations followed by [1,5]-sigmatropic rearrange-

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