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J. Mex. Chem. Soc. **2010**, *54(4),* 209-215
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ISSN 1870-249X

Theoretical Study of the Electronic Effects in the Intramolecular Ketene-Styrene [2+2] Cycloaddition

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Received August 12, 2010; accepted September 2, 2010

Abstract. DFT (B3LYP/6-31+G*) and post-Hartree-Fock (MP2/6-31+G*//B3LYP/6-31G*) calculations were carried out in order to explain the effect of a remote substituent in the intramolecular ketene-styrene [2+2] cycloaddition of *p*-substituted 2-methyl-7-aryl-hepta-1,6-dien-1-one which produces the bicycle[3.1.1] or the bicycle[3.2.0] heptanones according to Bèlanger experimental results. The transition state geometries were found as an asynchronous process with a three-member ring structure and an incipient positive charge development. Kinetic and thermodynamic controls were proposed at B3LYP/6-31+G* to determine which product is most likely to form in a competence reaction. In addition, the value of the ρ experimental reaction constant was reproduced, $\rho \sim -1.34$.

Keywords: B3LYP/6-31+G*, MP2/6-31+G*//B3LYP/6-31+G* calculations Hammett relationship, kinetic control, thermodynamic control, [2+2] cycloaddition.

Resumen. Se realizó un estudio teórico al nivel de teoría DFT (B3LYP/6-31+G*) y post-Hartree-Fock (MP2/6-31+G*//B3LYP/6-31G*) para explicar el efecto del sustituyente remoto en la cicloadición [2+2] intramolecular de cetena-estireno en 2-metil-7-arilhepta-1,6-dien-1-ona p-sustituida la cual produce biciclo[3.1.1] o biciclo[3.2.0] heptanonas de acuerdo a los resultados experimentales de Bèlanger. Se encontró que el estado de transición presenta una geometría de anillo de tres miembros, correspondiente a un estado de transición asincrónico por medio de una carga positiva incipiente. Se propone que la reacción puede ser controlada de forma cinética y termodinámica de acuerdo con los cálculos B3LYP/6-31+G*. Adicionalmente se reprodujo el valor de la constante de reacción experimental $p \sim -1.34$.

Palabras clave: B3LYP/6-31+G*, MP2/6-31+G*//B3LYP/6-31+G* relaciones tipo Hammett, control cinético, control termodinámico, cicloadición [2+2].

Introduction

The first examples of a ketene-alkene intramolecular [2+2] cycloaddition were reported in the 1960s [1]; however, in the early 1980s the systematic studies were reported and many different ketene-alkene [2+2] mechanisms have been proposed [2]. Only two of them are commonly accepted: a stepwise mechanism [3-5] and a concerted cycloaddition mechanism which could be highly asynchronous [2, 6-8] (Figure 1).

On the other hand, only intermolecular reactions of ketene-styrene cycloaddition, where the substituted styrenes are in *para* position, have been reported [9-10], whereas the first report on the intramolecular ketene-styrene cycloaddition was recently published in the literature by Bèlanger *et al.* [11]. In this report, two important conclusions can be accounted in the intramolecular ketene-alkene [2+2] cycloaddition: firstly, the regiochemistry of the cycloaddition is determined by the substitution pattern of the double bond [12], in which the more substituted internal alkene carbon will produce bicyclo[n.2.0]alkanones, while substrates in which the terminal alkene carbon is more substituted will give bicyclo[n.1.1]alkanones (Figure 2).

Secondly, the reaction yield will be higher with more nucleophilic alkenes. Furthermore, the influence of the electronic character of the substituted alkene in the cycloaddition reaction was modulated by a *p*-substituted aryl group in which only the bicycle[3.1.1] heptanone was produced as experimental observations with a particular regiochemistry has shown: *p*-substituted aryl group attached to the bicycle **1**, and the phenyl group attached to the bicycle **2** (Figure 3). The aryl attached to the bicycle is produced in higher yields by electrondonating (**ED**) groups than by electronwithdrawing (**EW**) groups [12-13]. Thus it was concluded by means of a Hammett study, that

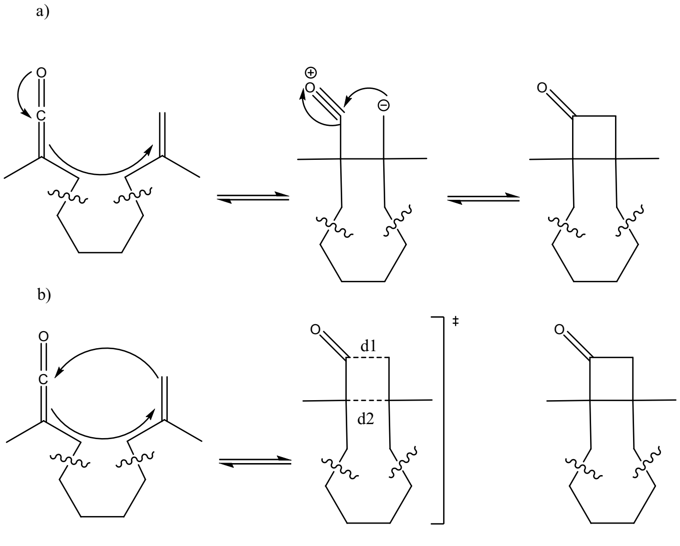


Figure 1. Reaction mechanisms paths accepted. a) A stepwise mechanism and b) concerted cycloaddition mechanism which could be highly asynchronous.

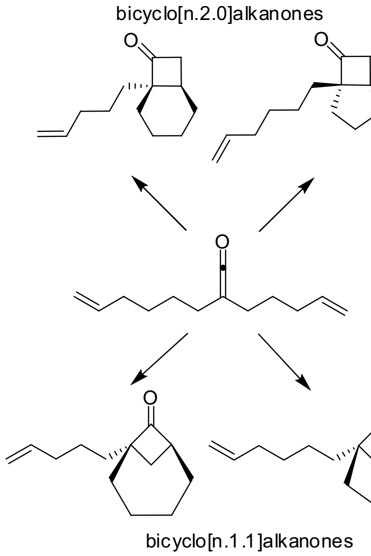


Figure 2. Four products in [2+2] cycloaddition are possible.

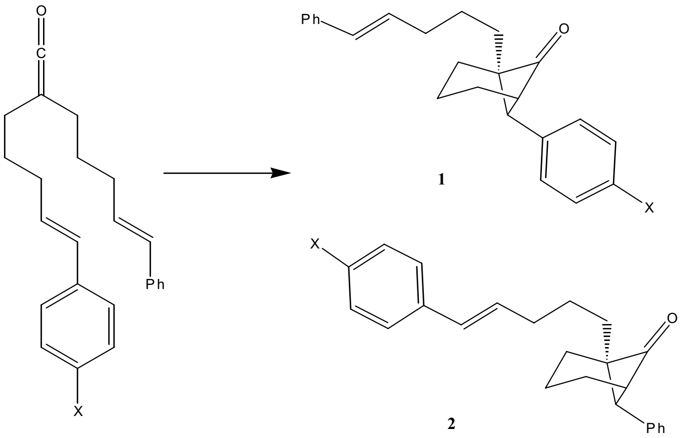


Figure 3. Bèlanger's model for electronic study on the remote position.

the reaction is accelerated by **ED** groups because of the determined value of $\rho = -1.39$ for this reaction in toluene [11].

In our previous work [6] we studied the intramolecular ketene-alkene [2+2] cycloaddition in 2-pent-4-enyl-octa-1,7-dien-1-one (Figure 2), and we determined by Hartree-Fock calculations (HF) at 6-31+G* basis and by Density Functional Theory (DFT) with the functional B3LYP at 6-31+G* basis calculations that the formation of bicyclo[n.2.0]alkanones are more stable than bicyclo[n.1.1]alkanones according to the Transition State (TS) analyses in an asynchronous process, forming a three-member ring structure. In spite of critical differences in HF and DFT methods, it is well known that both methods can lead to good approaching in TS studies, but the comparison of experimental results with HF or more complete and exact DFT help to complete a best understanding of in the mechanisms.

On the other hand, by calculating internal Molecular Orbitals (MO), the nucleophilic reactivity of the reaction is well-explained, but not the observed product. In order to complete this study, the electronic effect in the alkene moiety is necessary by taking a Hammett – TS –MO study into account.

In this context, Hammett's reactivity models are extremely useful as prediction tools for any reacting partner of known σ, σ^+ or σ^- substituent constant value [14-16]. In the case of σ, this value is defined by the relationship between the acidity constant of an X-substituted benzoic acid with respect to the unsubstituted benzoic acid. On the other hand, Hammett-Brown's σ^+ and σ^- constants were determined from the kinetics of hydrolysis of aryl substituted cumyl chlorides and the equilibrium reaction between substituted phenols and the corresponding phenolates [15]. A second parameter is the reaction constant (ρ, ρ^+ or ρ^-), which is related to the nature of the chemical reaction under a given set of conditions. The magnitude of this parameter measures the susceptibility of a reaction towards electronic effects [17], where positive or negative ρ values account for the reaction being favored by **EW** or **ED** substituent, respectively.

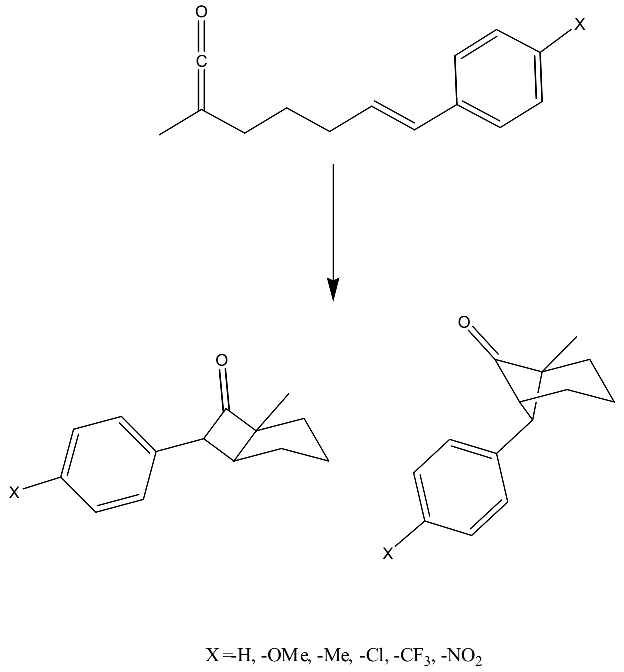
The σ parameter has been widely studied and being focused on the parameter for *para*-substituent σ_p, to split it into two distinct components: the inductive (or field) and the resonance contributions, σ_I and σ_R respectively, with $\sigma_p = \sigma_I + \sigma_R$ [18]. To quantify the inductive contribution, σ_I, various methods have been explored considering the composition of the ionization equilibrium of the compounds, in which the substituent is placed on a non-aromatic ring (bicyclooctane carboxylic acids or quinuclidines) [19-20].

The aim of this work is to establish the differences in the reaction mechanism to form bicycle[n.1.1] and bicycle[n.2.0] considering the electronic effect imposed by the 4-substituted aryl that drives to a particular reaction mechanism by finding a correlation between the calculated reaction energy versus σ_p or σ^+ substituent constants. The comparison between experimental and the theoretically calculated results enhance a best comprehension of this reaction.

Results and discussion

In order to develop a better comprehension on the electronic influence in the reaction, we performed this study with a simplified Bèlanger's model (Figure 4) in which the ketene is attached to the only (*p*-substituted)-phenylpent-4-enyl group as we are only founded in studying the [2+2] cycloaddition of ketene and styrene group. Ketenes are reactive intermediates; therefore, experimentally, the acyl chloride compounds are used to produce ketenes by deprotonation with triethylamine, at 393.15 K. Two possible products could be formed, the bicycle[3.1.1]heptanone or the bicycle[3.2.0]heptanone. Experimentally, it was found that bicycle[3.1.1]heptanone is a mixture of isomers [11] (Figure 3) depending on the nature of the X-substituent on the aryl group.

The relative energy was defined as the difference of electronic energy, corrected by Zero Point Energy (ZPE), between product and reactant (Table 1) of DFT and MP2



X = H, -OMe, -Me, -Cl, $-CF_3$, $-NO_2$

Figure 4. Simplified Bèlanger's model for electronic study on the remote position.

calculation levels. These results show that in the two kinds of calculations, the bicycle[3.2.0]heptanones are thermodynamically more stable than the bicycle[3.1.1]heptanones. Bicycle[3.2.0] energy values are in the range of −11.5 to −11.8 kcal/mole for B3LYP level and −29.5 to −30.0 kcal/mole for Møller-Plesset correction energy correlation truncated at second order (MP2), whereas the corresponding values for bicycle[3.1.1] are in the range of −5.8 to −6.3 kcal/mole for B3LYP level and −25.7 to −26.9 kcal/mole for MP2 level. The highest energy value was obtained with 4-NO_2 substituted bicycle[3.1.1], in which the electron-withdrawing feature exerted a certain influence on the thermodynamic stability. However, the MP2 energy is not the highest value for this compound, the electron-withdrawing effect is not observed in this kind of calculations.

The single point calculations were performed with MP2/6-31+G+//B3LYP/6-31+G*, they showed the stabilization of the electronic energy of products and they do not permit to discriminate clearly between an electron-withdrawing and electron-donating substituents.

Experimentally, the regiochemistry of cycloaddition is determined by the substitution pattern on the double bond [12-13]. Substrates in which the terminal alkene carbon is more substituted will result in bicyclo[n.1.1]alkanones. However, our ground state calculations show that the bicycle[3.2.0] is thermodynamically more stable than the bicycle[3.1.1], which is contrary to the experimental results. In this case, the temperature effect is not taken in consideration by the thermodynamic approximation [21] because the energy comparison was taken between two products that shown similar molecular structures and thermochemistry energies do not show a significant change.

On the other hand, Table 2 shows the relative energy in the transition state of both bicycle series. In general, the relative energy of bicycle[3.1.1] are less energetic than those of bicycle[3.2.0] at B3LYP calculations, i. e. in both case the bicycle[3.1.1]heptanone is more favorable to form than the bicycle[3.2.0]heptanone. The transition state geometry of each molecule studied is an asynchronous process with a three-

Table 1. Energies calculated of the reactant and products of [2+2] cycloaddition.

Substituent	Reactant		Bicycle[3.2.0]heptanone		Bicycle[3.1.1]heptanone	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
H	−618.330469[a]	−616.283991	−618.352600	−616.326975	−618.344586	−616.326836
	0.261972[b]		0.265386		0.266132	
	0.0[c]	0.0	−11.8	−30.0	−6.3	−26.9
Me	−657.648827	−655.455924	−657.670923	−655.503092	−675.662884	−655.496934
	0.289213		0.292771		0.293412	
	0.0	0.0	−11.7	−29.6	−6.2	−25.7
OMe	−732.856755	−730.478413	−732.878970	−730.525787	−732.870681	−730.521267
	0.2943643		0.297976		0.298697	
	0.0	0.0	−11.8	−29.7	−6.1	−26.9
Cl	−1077.926392	−1075.317899	−1077.948663	−1075.365087	−1077.940360	−1075.360713
	0.252122		0.255723		0.256454	
	0.0	0.0	−11.8	−29.6	−6.1	−26.9
CF_3	−955.391281	−952.567022	−955.413489	−952.613954	−955.405192	−952.609923
	0.266212		0.269767		0.270484	
	0.0	0.0	−11.8	−29.4	−6.2	−26.9
NO_2	−822.842680	−820.308797	−822.864437	−820.355781	−822.855968	−820.351254
	0.264310		0.267822		0.268491	
	0.0	0.0	−11.5	−29.5	−5.8	−26.6

[a]Electronic energy (hartrees), [b]Zero Point Energy (hartrees), [c]Relative energy (corrected by ZPE, $E_{product}$-$E_{reactant}$) (kcal/mole).

Table 2. Energies calculated of the transitions state of the [2+2] cycloaddition.

Substituent	Sigma Hammett[a] (Sigma +)[b]	Bicycle[3.1.1] (B3LYP)	Bicycle[3.2.0] (B3LYP)
H	0.00	−618.294387[c]	−618.281113
	(0.00)	0.262158[d]	0.261807
		22.8[e]	30.9
		−349.2576[f]	−236.9158
Me	−0.17	−657.613800	−657.599627
	(−0.31)	0.289517	0.289227
		22.2	30.9
		−350.7291	−234.0077
OMe	−0.27	−732.823492	−732.807770
	(−0.78)	0.294845	0.294496
		21.2	30.8
		−346.7979	−233.1654
Cl	0.23	−1077.890288	−1077.877392
	(0.11)	0.252443	0.252221
		22.8	30.8
		−359.7040	−245.8819
CF_3	0.54	−955.353447	−955.3421762
	(0.61)	0.266399	0.266245
		23.9	30.8
		−363.1330	−245.8819
NO_2	0.78	−822.804017	−822.79328
	(0.79)	0.264605	0.264445
		24.4	31.1
		−378.5776	−256.0684

[a]Reference [16], [b]included resonance effect, [c]Electronic energy (hartrees), [d]Zero Point Energy (hartrees), [e]Relative energy (corrected by ZPE, E_{TS}-$E_{reactant}$) (kcal/mole), [f]negative vibrational frequency with the largest contribution from internal coordinates involved in the reaction. All calculations were performed with 6-31+G* basis.

member ring structure as Ramirez-Galicia *et al.* [6] and Wang *et al.* [22] have found.

Houk *et al.* [23] proposed that kinetic and thermodynamic controls could be established from the difference of the activation energy between two competitive reactions; thus, the kinetic control has an energy difference of 5-10 kcal/mole while the thermodynamic control has an energy difference of 1-5 kcal/mole. By considering the aforementioned data, a plot of differences in activation energy values at B3LYP/6-31+G* levels between bicycle[3.2.0] and bicycle[3.1.1] heptanones and the corresponding substituent constant σ_p Hammett and σ_p^+ Hammett-Brown are showed in Figure 5A and Figure 5B. In both cases, the B3LYP results showed that all substituents follow the kinetic control at transition state, because the energy difference between both bicycles is higher than 5 kcal/mole (Figure 5A and Figure 5B); this behavior is in concordance with the formation of bicycle[3.1.1], the kinetic product, which is observed in the experimental results.

Figure 6 also shows the relationship of the electronic energy differences in the transition state calculated by B3LYP/6-31+G* as function of $\log(k_X/k_H)$, the correlation coefficient (R) value is 0.977 (continue line) included all substituents, in this case the –OMe substituent is also out the trend, and when this substituent was excluded from the relationship, the R value increases up to 0.997 (dash line), this result also suggests that the resonance effect over-stabilizes the transition state by 0.7 kcal/mole.

A best linear relationship is achieved by the –OMe exclusion independent of the level of calculation. The electronic correlation influence is observed in these calculations because the magnitude of slope in the linear relationship changes considerably when the calculations were performed by B3LYP functional.

A possible linear free energy relationship (LFER) can be established from Figure 6. This relationship, from the Arrhenius equation, can be expressed as follow:

$$\log\left(\frac{k_X}{k_H}\right)=\left(\frac{\log e}{RT}\right)(-(E_X-E_H))^{\neq}$$

where k_x and k_H are the reaction rate constants of X-substituent and hydrogen substituent respectively and $\left(\frac{\log e}{RT}\right)$ is proportional to the slope calculated from the second relationship

$$B\left(\frac{\log e}{RT}\right)=m$$

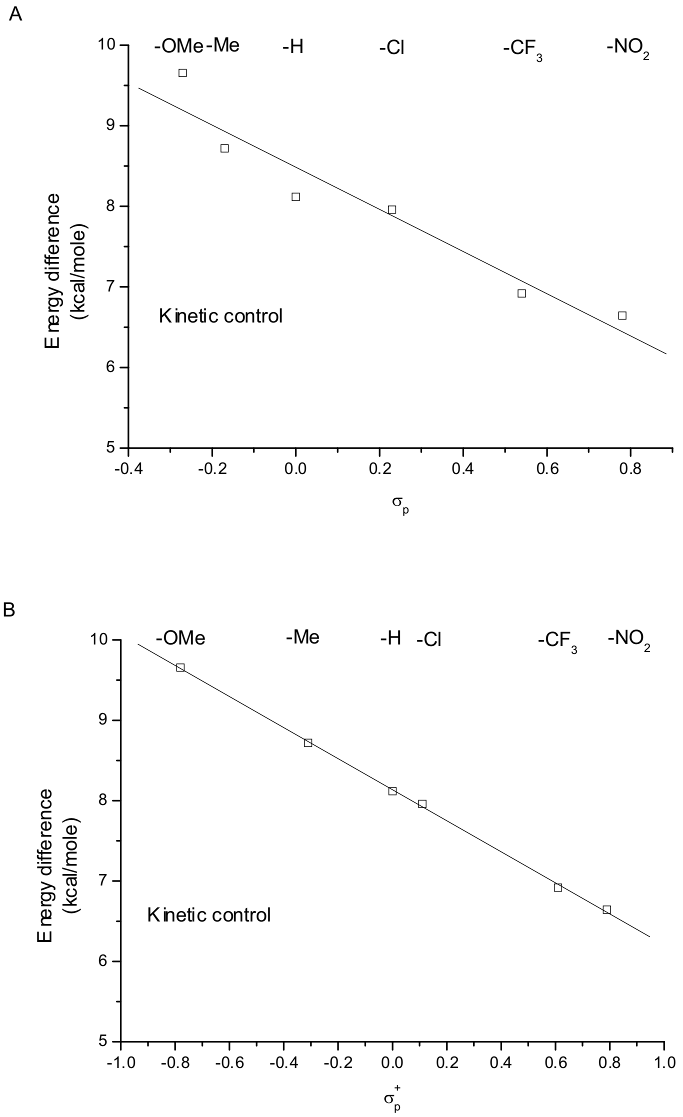


Figure 5. Kinetic control of the studied molecules calculated by B3LYP. A) Hammett relationship, the linear regression is $\Delta E^{B3LYP} = -2.61855\ (\pm 0.36902)\ \sigma_p + 8.48626\ (\pm 0.15472)$; R = 0.9625, SD = 0.34009, N = 6, P = 0.00208. B) Hammett-Brown relationship, the linear regression is $\Delta E^{B3LYP} = -1.93175\ (\pm 0.02607)\ \sigma_p + 8.13706\ (\pm 0.01393)$; R = 0.99964, SD = 0.03383, N = 6, P < 0.0001.

where *B* indicates the over-estimation of the activation energy from the transition energy. For the relationships without –OMe substituent, B_{B3LYP} is 2.371, i.e. the transition electronic energy is 2.4 times higher than the experimental activation energy for B3LYP calculations; therefore, an excellent correlation was obtained. Previously, Ramírez-Galicia *et al.* [6] have estimated the transition electronic energy with HF and DFT methods for bicycle[3.1.1]heptanone as 46.5 and 28.0 kcal/mole respectively, without changing the reaction mechanism. The conclusion was that the electronic correlation stabilizes the transition states around 20 kcal/mole. It is clear that when a high electronic correlation method is used a better estimation of the activation energy is obtained. In these calculations, the electronic correlation stabilizes also the transition states around 20 kcal/mole (Table 2).

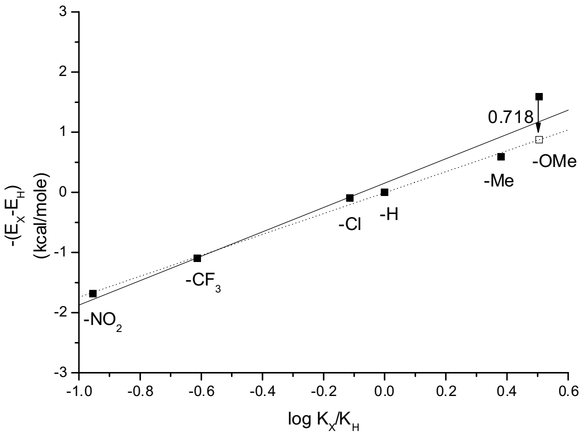


Figure 6. Electronic energy difference in the transition state correction calculated by B3LYP, dashed line included the –OMe substituent: $-\Delta E_{B3LYP} = 0.1526\ (\pm 0.11838) + 2.02563\ (\pm 0.22248) \log k_X/k_H$; R = 0.97671, SD = 0.28082, N = 6, P = 8.07117×10^{-4}, continue line excluded the –OMe substituent, $-\Delta E_{B3LYP} = -0.00525\ (\pm 0.03863) + 1.7381\ (\pm 0.0719) \log k_X/k_H$; R = 0.99744, SD = 0.07559, N = 5, P = 1.55149×10^{-4}.

The differences in the electronic energy of the transition states (E_X-E_H) were modified dividing these values between the relationship slopes without –OMe substituent, $m_{B3LYP} = 1.7381$, in order to represent the experimental transition energies. Using these modifications, a Hammett relationship was plotted (Figure 7). Two linear relationships are included, in a continue line the –OMe substituent was included and in the dash line the –OMe substituent was excluded.

Connors suggested that a linear Hammett correlation have to exceed an R value of 0.95 [24]. In this sense, both linear relationships satisfy this condition of linearity (see figure caption Figure 7). However, in the linear relationships where the –OMe substituent was included, it is clear that this substituent continues out of the trend in spite of the energy correction, it is expected that his electronic energy difference would be around 0.5 kcal/mole (Figure 7).

On the other hand, when the –OMe substituent was excluded from the linear relationships, R increase to 0.984 for B3LYP corrected energies respectively (see figure caption Figure 7). The slopes in these equations are the reactions constants; the value is $\rho_{B3LYP}{}^{mod} = -1.34$, these results are closer to the experimental Hammett relationship $\rho_{exp} = -1.39$, i. e., the correction in the electronic difference energy allows us to reproduce the experimental value of ρ.

During the asynchronous TS of the [2+2] cycloaddition, an incipient positive charge is developed (Figure 8A) in the less substituted carbon of the alkene group of the –OMe substituent. In this context, a best correlation of the electronic energy differences of the transition states as a function of Hammett-Brown's σ^+ is depicted (Figure 9). It is important to mention that the strong **ED** groups such as –NO_2 and –CF_3

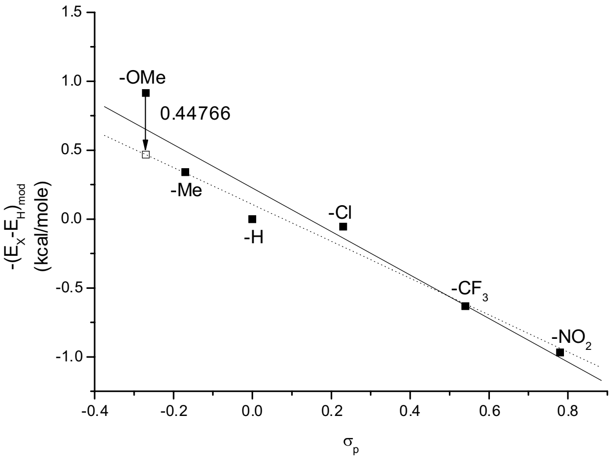


Figure 7. Hammett relationship calculated by B3LYP, dashed line included the –OMe substituent, ΔE_{B3LYP} = 0.22526 (±0.08877) −1.57839 (±0.21172) σ_p; R = 0.96585, SD = 0.19512, N = 6, P = 0.00173, continue line excluded the –OMe substituent ΔE_{B3LYP} = 0.10628 (±0.06098) −1.33858 (±0.13761)σ_p; R = 0.98452, SD = 0.10667, N = 5, P = 0.00231.

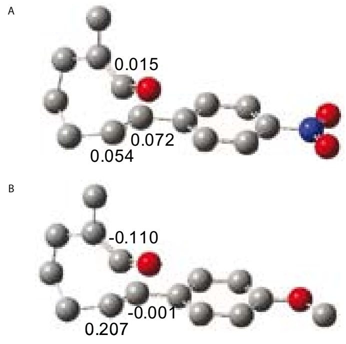


Figure 8. Mulliken charges in the cycle of tricycle transition state for A) –OMe and B) –NO_2 substituents.

(Table 2) have similar σ_p and σ_p^+ values. Thus, theses groups did not develop an incipient positive charge (Figure 8B).

High correlations of electronic energy differences modified with σ^+ were found without excluding any substituent and their reaction constant is $\rho^+{}_{B3LYP}{}^{mod}$ = −1.16. It is clear that the reaction constant for B3LYP level does not reproduce the experimental value in these conditions in spite of the correlation coefficient close to the unit. On the other hand, the arenium ion is stabilized by the electronic assistance of the oxygen to TS center by a quinonoidal resonance structure in the case of **ED** groups as –OMe (Figure 8B).

The B3LYP functional does not guarantee that the reaction mechanism drives by an incipient positive charge in the reaction center. On the other hand, the electronic energy of –OMe substituent in the transition state could be overestimated in both level of calculations in spite of the correction made because this substituent is out of trend. Linear correlations between σ_p and ΔE without –OMe substituents reproduce the experimental behavior.

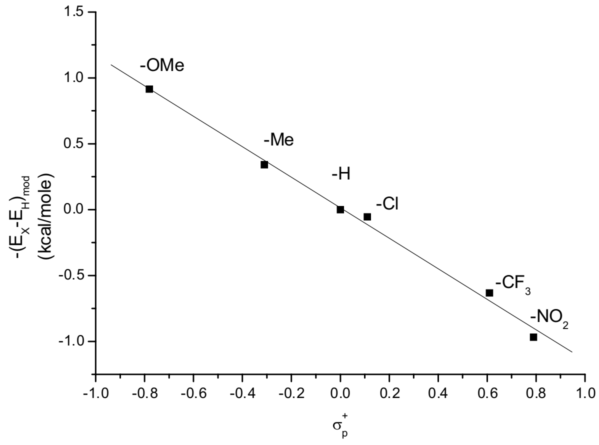


Figure 9. Hammett-Brown σ^+ relationship calculated by B3LYP, all substituents are included in the relationship -ΔE_{mod} = 0.01428 (±0.02345) - 1.15747 (±0.04389)σ_p^+; R = 0.99714, SD = 0.05695, N = 6, P < 0.0001.

Conclusions

The [2+2] cycloaddition mechanism was performed by a simplified model of Bèlanger' studies, where two possible products, the bicycle[3.2.0]heptanones and the bicycle[3.1.1]hept anones, could be formed. The B3LYP calculation has shown that bicycle[3.2.0]heptanones are the most stable in striking contrast to the experimental observations. A kinetic control has been found responsible for the experimental results.

On the other hand, the electronic transition energy calculated by B3LYP levels with 6-31+G* is over-estimated by a factor of 2.4 times; it is well known that the electronic correlation stabilizes this energy, for example, the single point calculations with MP2/6-31+G*//B3LYP/6-31+G* showed the stabilization of the electronic energy of the products, however this result does not permit to discriminate clearly between an electron-withdrawing and electron-donating substituents. Using this over-estimation factor, it is possible to establish a Hammett relationship with both level of calculations and Hammett-Brown relationship. Therefore, the Hammett relationship is the most correct representation of experimental results by a theoretical way.

Finally, a combination of the inductive and resonant effect could be responsible for the atypical behavior of the –OMe substituent on the trend of the electronic transition energies and in the Hammett and Hammett-Brown relationships.

Experimental part (Calculation method)

All calculations presented here were performed with a Gaussian 03 molecular orbital package [25]. Geometry optimizations and frequency calculations were carried out with B3LYP/6-31+G* [26-27]. The vibrational frequencies calculated for all the systems studied confirmed the nature of the stationary points (for minimum energy all positive frequencies, for transition states one imaginary frequency with the largest contribution from internal coordinates involved in the reaction). Vibrational frequencies were scaled by a standard factor of 0.9614 for B3LYP functional [28] considering the zero-point energy. Additionally, the post-Hartree-Fock MP2 calculations [29-30] were performed at the single point level taking from B3LYP/6-31+G* geometry.

Acknowledgements

Dr. R. Garduño-Juárez (Instituto de Ciencias Físicas, UNAM) is acknowledged for using his computer facilities and software. GRG would like to thank Dra. M. Poisot for her comments.

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