Structural and Solvent Effects on the Mechanism of the Thermal Decarboxylation of 2-Oxetanones. A Limiting Case between Concerted and Stepwise Pathways in Pericyclic Reactions

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Abstract: The thermal decarboxylation of 2-oxetanones (β-lactones) to yield alkenes has been studied using *ab initio* SCF-MO computational methods. Solvent effects have also been taken into account. The reaction is predicted to be concerted in the gas phase, the corresponding transition structures having non-Woodward−Hoffmann topologies. A set of 10 substituted 2-oxetanones has been studied, and it has been found that donating groups (methyl, vinyl, phenyl) at C4 facilitate the [2+2] cycloreversion. The saddle points which connect substrates and products are predicted to be highly polar in nature, and, therefore, even moderately polar solvents such as *o*-dichlorobenzene accelerate the reaction. *trans*-2-Oxetanones are predicted to react faster than their *cis* isomers if solvent effects are taking into account. Self-consistent reaction field methods based on multipole expansions of the free energy of solvation tend to overestimate the stability of zwitterionic intermediates at the Hartree−Fock level. This results in stepwise mechanisms in several cases, although higher levels of theory predict again concerted mechanisms.

Introduction

The thermal decarboxylation of 2-oxetanones (eq 1) constitutes a well-established method for the synthesis of alkenes.[1] This reaction can be extended to the chemical synthesis of allenes *via* thermal decarboxylation of 3-alkylidene-2-oxet-

$$(1)$$
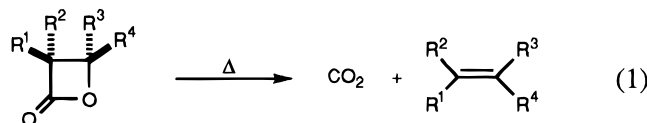
anones[2] (eq 2). From a historical perspective, it is noteworthy that this process was proposed in 1880 by Erlenmeyer,[3] even before the first 2-oxetanone was synthesized and characterized

$$(2)$$
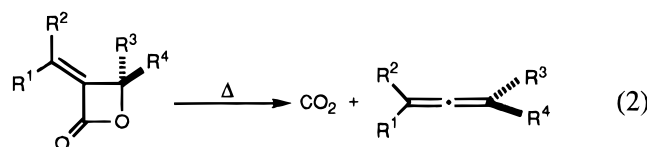
by Einhorn.[4] The reaction, which can be considered as [2+2] thermal cycloreversion, possesses three favorable features: first, the process is simple to perform since the by-product is a gas which escapes from the reaction mixture. Second, the stereocontrol is virtually complete, and with very few exceptions (*vide*

infra) the decarboxylation takes place with retention of configuration. Third, the substrates, namely, 2-oxetanones, are in turn readily available and can be synthesized by means of many different procedures.[1a,5] In this respect, perhaps the most interesting methods are those which involve a convergent coupling between carbonyl compounds and ketenes[5a,6] or lithium enolates prepared from the corresponding thioesters.[2a,7]

Given the advantages mentioned above, it is therefore not surprising that the decarboxylation of 2-oxetanones has proved to be very useful in the synthesis of alkenes not readily accessible by other methods. Thus, the reaction has been applied to the synthesis of α-haloalkenes,[8] substituted enol ethers,[9] steroids,[10] heterocycles,[11] terpenes,[12] sterically congested or strained olefins,[13] allyl silanes,[14] substituted arene oxides,[15] and chiral 4-ethylidene cyclohexanes.[16]

From a mechanistic standpoint, this reaction is also very interesting, since thermal [2+2] cycloadditions (or cycloreversions) are much less common than pericyclic reactions involving

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six π-electrons.[17] According to the Woodward–Hoffmann rules,[18] [2+2] processes are thermally allowed *via supra–antara* topologies in the corresponding transition structures. In the case of thermal [2+2] cycloadditions of double bonds and cumulenes, the highly demanding *supra-antara* geometry can be avoided *via* stepwise mechanisms, as it occurs in the cycloaddition between ketenes and imines[19] or in certain [2+2] cycloadditions between activated isocyanates and alkenes.[20] Another possibility is the $[_\pi 2_s + (_\pi 2_s + _\pi 2_s)]$ mechanism, which has been proposed for the reaction between allenes and alkenes,[21] as well as between ketenes and alkenes[22] or carbonyl compounds.[23]

Within the context described above, it is rather surprising that, to the best of our knowledge, only two papers devoted to computational studies on the mechanism of this reaction have been published to date. In the first one, Yamabe *et al.*[24] carried out a MNDO study on the thermal decarboxylation of several 4-substituted 2-oxetanones and β-propiolactone itself. These authors concluded that the thermal decarboxylation of 2-oxetanones should take place in a concerted, although asynchronous, manner, *via* transition structures such as **TS** (see Scheme 1, mechanism a), in which the coplanar arrangement of the 2-oxetanone ring is retained. More recently, Pericàs *et al.*[25] reported a more elaborated study using the AM1 semiempirical Hamiltonian. These authors proposed a similar mechanism, and observed that the asynchronicity of the reaction correlates well with the energy of activation; *i.e.*, the more asynchronous the cycloreversion is, the lower the activation barrier. Another interesting conclusion of this paper is that the transition structures have no diradical character. Finally, it is noteworthy to mention that the aforementioned papers refer exclusively to the gas phase.

Apart from the computational studies, several authors have proposed different mechanistic models to explain their experimental results. Thus, nonplanar *supra–antara* (Scheme 1, mechanism b) transition structures have been proposed by Nishida *et al.*,[26] in agreement with the classical Woodward–Hoffmann mechanism. However, many experimentalists have proposed a two-step mechanism, (Scheme 1, mechanism c) in which the O1–C4 bond is broken *via* transition structure **TS1** to form an intermediate **INT**. The second step consists of the extrusion of CO_2 by means of the C2–C3 bond cleavage,

Scheme 1[a]
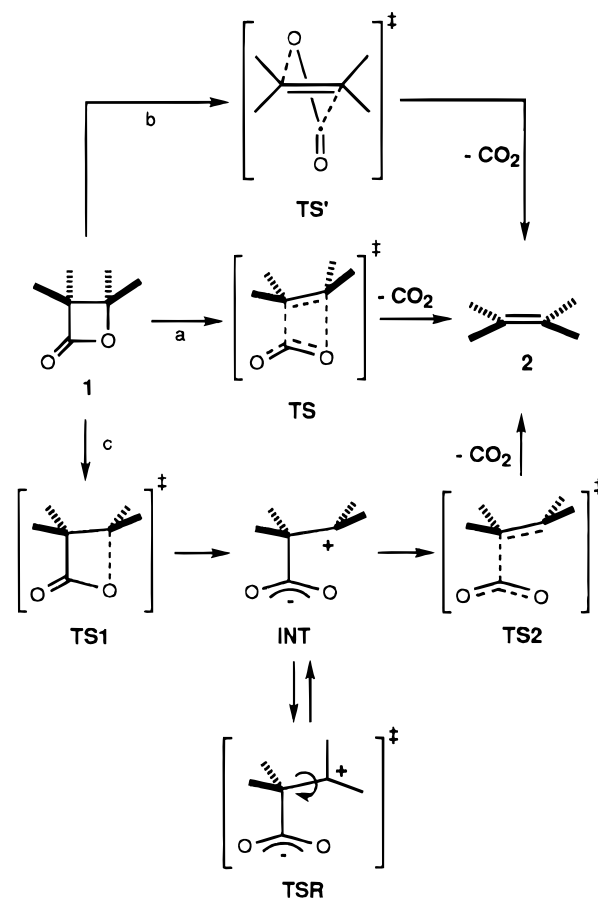
[a] The possible substituents at the different positions are not specified.

through the transition structure **TS2**. Four arguments have been proposed in favor of this latter mechanism. (i) The reaction has a pronounced solvent effect,[27] polar solvents accelerating the decarboxylation. (ii) The reaction has a negative volume of activation.[28] (iii) *trans*-2-Oxetanones react faster than the *cis* isomers.[26] This observation is opposite to that reported for the cycloaddition between ketenes and olefins, a process which is described to a concerted $[_\pi 2_s + _\pi 2_a]$ or to a $[_\pi 2_s + (_\pi 2_s + _\pi 2_s)]$ mechanism. (iv) It has been reported that, in very few cases,[29–31] the decarboxylation is not stereospecific. Thus, in 1980 Mulzer *et al.*[29] found that thermolysis of *cis*-4-aryl-3-substituted-2-oxetanones in 1,2-dichlorobenzene takes place stereospecifically for 3-methyl, 3-ethyl, and 3-isopropyl β-lactones. However, in the case of the 3-*tert*-butyl analogue, 9% of the *trans* olefin was obtained after heating at 140 °C. However, in a paper which appeared 1 year later, the same authors[30] reported that the decarboxylation of *cis*-4-phenyl-3-*tert*-butyl-2-oxetanone takes place stereospecifically to yield the corresponding *cis* olefin in 1,2-dichlorobenzene at 100 °C, provided that the reaction was carried out in the absence of Lewis acids.

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It is noteworthy that the majority of the arguments against concerted mechanisms correspond to reactions performed in solution. However, these arguments are ambiguous. For example, a significant solvent effect in favor of polar solvents is compatible with zwitterionic intermediates such as **INT**, but also with highly polar transition structures such as **TS** or **TS′**, provided that the charge separation in those saddle points was large enough. A stepwise mechanism allows a loss in stereo-control *via* transition structures such as **TSR** (Scheme 1). However, if **TS2** is lower in energy than **TSR**, the stepwise mechanism is also compatible with the retention of configuration usually observed.

In conclusion, from the experimental evidence available the mechanism of the thermal decarboxylation of 2-oxetanones is not clear. Within this context, we report herein the first computational study on this reaction which uses high-level *ab initio* methods. In addition, we have performed our study not only in the gas phase, but also in solution, given the importance of the solvent in this particular thermal cycloreversion.

Computational Methods

All the results presented in this work have been obtained using *ab initio* MO theory, by means of the GAUSSIAN 92,[32] GAUSSIAN 94,[33] and GAMESS[34] series of programs, with the standard 6-31G* and 6-31+G* basis sets.[35] Geometry optimizations have been carried out at the Hartree−Fock (HF) level, and in several representative cases these optimizations have been performed at the second-order Møller−Plesset (MP2) level keeping the core electrons frozen.[35] For larger systems in which electron correlation was expected to be critical in order to evaluate properly the reaction profile, we used Density Functional Theory[36] (DFT). We carried out these calculations by means of the hybrid functional developed by Becke, which is customarily denoted as B3LYP.[37] Zero-point vibrational energies (ZPVE) were scaled by 0.89[38] when computed at the HF/6-31+G* level. Stationary points were characterized by frequency calculations.[39] All reactants, intermediates, and products have positive defined Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration. Atomic charges[40] were calculated with

the natural bonding analysis (NBA) method.[41] In some cases, single-point energies were computed up to MP4SDQ and QCISD(T) levels. For the parent reaction, G2(MP2)[42] and CASSCF[43] calculations were performed.

Nonspecific solvent effects were partially taken into account by means of the continuum models.[44] These models, although approximate, have been used in the study of other cycloadditions[45] and have provided results in qualitative agreement with experimental results. In these models, the solvent is described by its macroscopic dielectric relative permittivity ϵ. The solute is placed in a cavity created in the continuum, at the cost of spending out some cavitation energy. The electronic distribution of the solute polarizes the continuum which generates an electric field inside the cavity which in turn affects the solute's geometry and electronic structure. If the free energy of solvation is approximated by this polarization scheme, the energy of the solute can be approximately evaluated by solving the nonlinear Schrödinger equation

$$[\hat{H}^\circ + V_{\text{int}}]|\psi\rangle = E|\psi\rangle \qquad (3)$$

in which $\hat{H}^\circ$ is the usual gas-phase Hamiltonian, and V_{int} is approximated by a multipole expansion in the form[46]

$$V_{\text{int}} = -\sum_{l,l'=1}^{\infty} \sum_{m,m'=-l,l'}^{+l,l'} M_l^m f_{l,l'}^{m,m'} \langle\psi|M_{l'}^{m'}|\psi\rangle \qquad (4)$$

where M_l^m represents the (l,m) component of the multipole expansion of the solute evaluated at the center of the cavity, and the $f_{l,l'}^{m,m'}$ terms are called reaction field coefficients and only depend upon the geometry cavity and the properties of the continuum. For the case of an ellipsoidal cavity with three independent axes oriented with respect to the principal axes of inertia of the solute, analytical expressions for the solvation energy and for their derivatives with respect to the nuclear coordinates are available.[47] It is shown that in an ellipsoidal cavity the convergence in the multipole expansion is faster than in a spherical one,[48] and, therefore, reasonable estimates of the solvation energy are achieved at $l_{\text{max}} = 6$. In this paper, we shall denote this SCRF methods as L6A3 ($l_{\text{max}} = 6$, ellipsoidal cavity with three independent axes). This model has been applied to the reaction under study using a locally modified version of the GAUSSIAN 92 program suite to incorporate the SCRFPAC link.[49]

If expansion 4 is truncated at $l_{\text{max}} = 1$ and a spherical cavity is considered, eq 4 becomes

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$$V_{int} = -\mathbf{g}\boldsymbol{\mu}\langle\psi|\mu|\psi\rangle \tag{5}$$

where $\boldsymbol{\mu}$ is the dipole moment and $\mathbf{g}$ is now the reactive field, which is simply evaluated as the quantity

$$\mathbf{g} = \frac{2(\epsilon - 1)}{2\epsilon + 1}\frac{1}{a_0^3} \tag{6}$$

where a_0 is the spherical cavity radius. In this paper, we shall denote this more simple SCRF approach as L1A1 ($l_{max} = 1$, spherical cavity). Wiberg *et al.*[50] have implemented this model in the GAUSSIAN 92 and GAUSSIAN 94 suites, and it is usually cited as the Onsager model.

An alternative SCRF approach consists in the Polarizable Continuum Model (PCM) developed, among others,[44] by Tomasi *et al.*[51] According to this model, the polarization is a function of charge density $\sigma_p(\mathbf{r_s})$ in the form

$$\sigma_p(\mathbf{r_s}) = -\left(\frac{\epsilon - 1}{4\pi\epsilon}\right)\mathbf{E}(\mathbf{r_s})\mathbf{n}(\mathbf{r_s}) \tag{7}$$

where $\mathbf{n}$ is an unitary vector pointing outward the surface, $\mathbf{r_s}$ is a point of the cavity surface, and $\mathbf{E}(\mathbf{r_s})$ is the total electric field. The solute−solvent interaction can be expressed in terms of σ_p by integration over the solute's surface S. Thus, for a given molecular distribution of n electrons and N nuclei, V_{int} can be written as

$$V_{int} = \sum_i^{n,N} \xi_i \int_S \frac{\sigma_p(\mathbf{r_s})\,d\mathbf{r_s}}{|\mathbf{r_i} - \mathbf{r_s}|} \tag{8}$$

where $\xi_i = -1$ for the electrons and $\xi_i = +Z_i$ for the nuclei. The different PCM approaches differ in the definition of the cavity. In PCM itself, this surface is generated from overlapping spheres centered over the different nuclei. In the IPCM approach, the cavity is a static gas-phase isodensity surface, and in the SCI-PCM this isodensity surface is self-consistent.[52] The isosurface value is 0.0004 au, which yields molar volumes in good agreement with the experimental ones. This latter method has been implemented in the GAUSSIAN 94 code by Wiberg *et al.*[52] and allows geometry optimizations.

The calculations reported in this work have been carried out for *o*-dichlorobenzene ($\epsilon = 9.93$), a very common solvent for this kind of reactions.
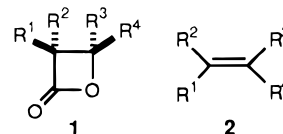
Results and Discussion

Gas-Phase Calculations. We have selected the β-lactones depicted in Figure 1 as representative examples of the 2-oxetanones for which experimental data concerning energies and stereochemistry are available. First, the parent reaction, namely, the thermal decarboxylation of 2-oxetanone **1a** to yield ethylene **2a** and carbon dioxide, was explored at several theoretical levels. The energies of activation and reaction, as well as the reaction enthalpies obtained, are collected in Table 1. To the best of our knowledge, two experimental studies on this parent reaction have been published to date.[53,54] In the most recent paper, Frey and Pidgeon[53] studied the **1a** → **2a** + CO_2 reaction in the gas phase in the temperature range 262−322 °C. These authors have found a strong dependence of the Arrhenius parameters on the method of extrapolation. Thus, for the log k *vs* $p^{-0.5}$ and k^{-1} *vs* $p^{-0.5}$ extrapolations, they obtained the extreme values of 41.98 and 44.70 kcal/mol for the activation energy. The value

(50) (a) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 523. (b) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

(51) (a) Tomasi, J.; Bonaccorsi, R.; Cammi, R.; Olivares del Valle, F. J. *J. Mol. Struct. (THEOCHEM)* **1991**, *234*, 401. (b) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (c) Miertus, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239. (d) Cammi, R.; Tomasi, J. *J. Comput. Chem.* **1995**, *16*, 1449.

(52) (a) Wiberg, K. B.; Castejon, H.; Keith, T. A. *J. Comput. Chem.* **1996**, *17*, 185. (b) Wiberg, K. B.; Keith, T. A.; Frisch, M. J.; Murcko, M. *J. Phys. Chem.* **1995**, *99*, 9072. (c) Wiberg, K. B.; Rablen, P. R.; Rush, D. J.; Keith, T. A. *J. Am. Chem. Soc.* **1995**, *117*, 4261.

(53) Frey, H. M.; Pidgeon, I. M. *J. Chem. Soc., Faraday Trans. 1*, **1985**, *81*, 1087.

Figure 1. 2-Oxetanones **1** and alkenes **2** included in this work. The same substitution patterns apply to the transition structures and intermediates depicted in Scheme 1.

Table 1. Activation Energies[a] (ΔE_a, kcal/mol), Energies of Reaction,[a] and Enthalpies of Reaction (ΔE_{rxn} and ΔH_{rxn}^{298}, Respectively, kcal/mol) of the Thermal Decarboxylation of 2-Oxetanone **1a**

method	ΔE_a	ΔE_{rxn}	ΔH_{rxn}^{298}
exp[b]	43.11($\pm$0.76)		
exp[c]	45.81($\pm$0.07)		−2.50
exp[d]			−14.10
HF/6-31G*	51.00	−19.43	−18.41
HF/6-31+G*	49.50	−20.59	−19.55
MP2/6-31+G*//HF/6-31+G*	41.97	−14.27	−14.53
MP2/6-31+G*	41.67	−15.54	−14.21
MP2/6-31++G**	41.66	−16.29	−15.03
B3LYP/6-31+G*	36.93	−14.64	−13.18
G2(MP2)	39.64	−15.68	−18.63

[a] Zero-point vibrational energies corrections, computed at the level of geometry optimization and appropriately scaled, are included. [b] Experimental value taken from ref 53. [c] Experimental value taken from ref 54. [d] Experimental value taken from ref 55.

of 43.11 kcal/mol included in Table 1 corresponds to their best estimate. This value is slightly lower than that previously obtained by James and Wellington[54] (see Table 1). From the thermochemical data reported in the literature,[55] the experimental enthalpy of reaction is −14.1 kcal/mol. The value of $\Delta H_{rxn}^{298} = -2.5$ kcal/mol suggested in ref 54 seems to be less accurate. As it can be seen from the data reported in Table 1, the agreement between our computed energies of activation and that obtained by Frey and Pidgeon is reasonably good. Indeed, this agreement is achieved at the MP2/6-31+G*//HF/6-31+G* level. Further improvement in the quality of the basis set and/or in the theoretical level does not result in a better agreement. The same conclusion can be extended to the ΔH_{rxn}^{298} values (see Table 1).

Our calculations suggest that the **1a** → **2a** + CO_2 reaction is concerted in the gas phase. The shape of the transition structure

(54) James, T. L.; Wellington, C. A. *J. Am. Chem. Soc.* **1969**, *91*, 7243.

(55) The values used in our evaluation of ΔH_{rxn}^{298} are those reported in the following referenes: Cox, J. O.; Pilher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. R.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.
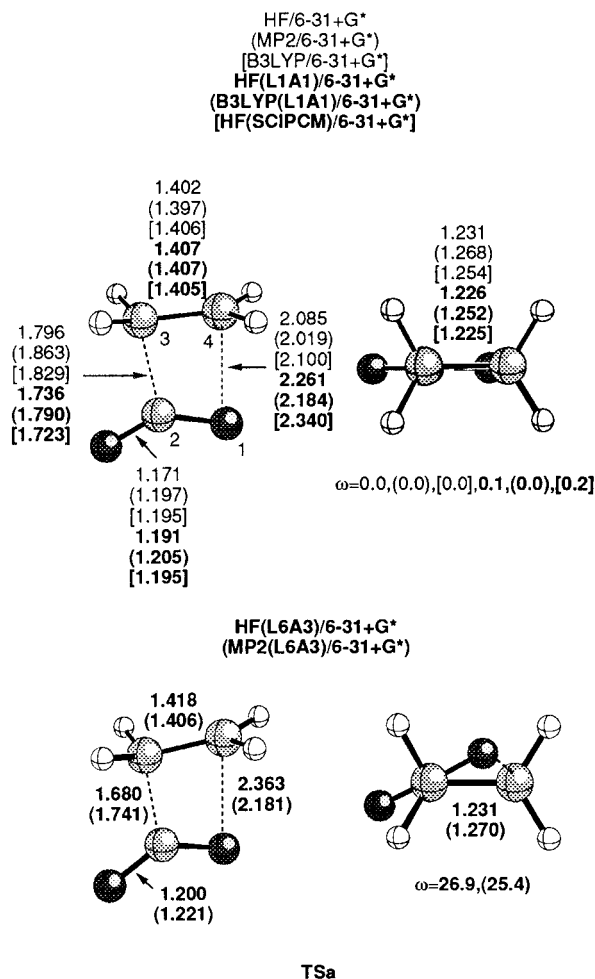
HF/6-31+G*
(MP2/6-31+G*)
[B3LYP/6-31+G*]
HF(L1A1)/6-31+G*
(B3LYP(L1A1)/6-31+G*)
[HF(SCIPCM)/6-31+G*]

1.402
(1.397)
[1.406]
1.407
(1.407)
[1.405]

1.231
(1.268)
[1.254]
1.226
(1.252)
[1.225]

1.796
(1.863)
[1.829]
1.736
(1.790)
[1.723]

2.085
(2.019)
[2.100]
2.261
(2.184)
[2.340]

1.171
(1.197)
[1.195]
1.191
(1.205)
[1.195]

ω=0.0,(0.0),[0.0],**0.1**,**(0.0)**,**[0.2]**

HF(L6A3)/6-31+G*
(MP2(L6A3)/6-31+G*)

1.418
(1.406)

1.680
(1.741)

2.363
(2.181)

1.231
(1.270)

1.200
(1.221)

ω=26.9,(25.4)

TSa

Figure 2. Ball-and-stick representation of **TSa,** associated with the thermal decarboxylation of 2-oxetanone **1a.** Bond distances and angles are given in Å and deg, respectively; ω is the dihedral angle formed by the O1, C2, C3, and C4 atoms. In this and the following figures which incorporate ball-and-stick representations, unless otherwise noted, atoms are represented by increasing order of shading as follows: H, C, O.

TSa located at several levels of theory is depicted in Figure 2. As it can be seen in **TSa,** the cleavage of the O1—C4 bond is more advanced than that corresponding to the C2—C3 bond. The most important feature of **TSa** is that it has C_s symmetry, with a dihedral angle ω = O1—C2—C3—C4 of 0.0° at all the theoretical levels studied by us. This non-Woodward—Hoffmann geometry can be understood observing the interaction diagram corresponding to the frontier orbitals of ethylene and carbon dioxide, depicted in Figure 3. Thus, interaction between a properly oriented E''_{2g} orbital of CO_2 and the LUMO of ethylene leads to a nonbonding interaction between C2 and C3 and an in-phase interaction between O1 and C4. The canonical MO corresponding to this combination is the HOMO-2 of **TSa,** as it can be seen in Figure 4. On the other hand, the interaction between the HOMO of ethylene and the unoccupied E'_{1u} MO of CO_2 leads to an in-phase interaction between C2 and C3, and to a dislocation between O1 and C4. The MO corresponding to this latter combination is the HOMO of **TSa** (Figure 4). Therefore, the larger bond distance between the O1 and C4 atoms results from the equilibrium between these two opposite interactions.

An alternative explanation for the feasibility of this non-Woodward—Hoffmann saddle point can be provided by the extended Hückel—Möbius model recently proposed by Herges.[56]

(56) Herges, R. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 255.

(A)

E (a.u.)

E'_{1u}

(LUMO)

B''_{2g}

(LUMO)

Ⓑ

Ⓐ

(HOMO)

(HOMO)

E''_{2g}
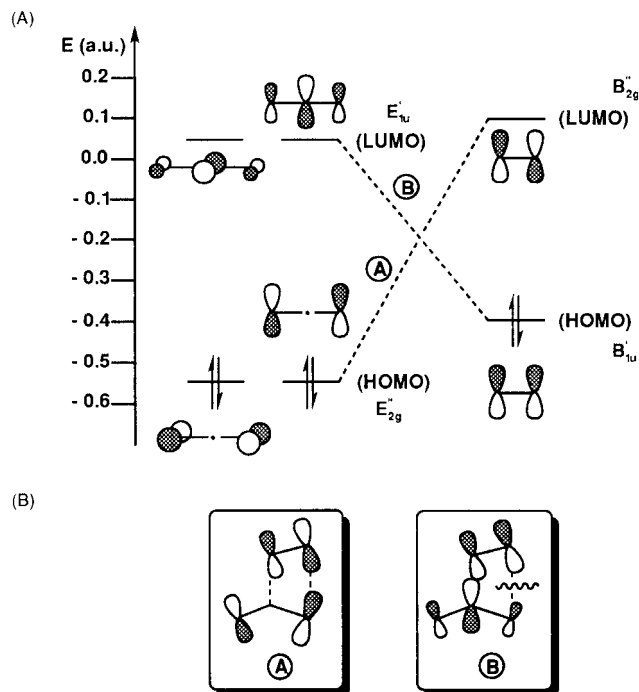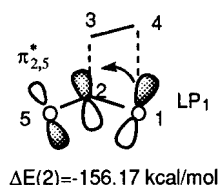
B'_{1u}

(B)

Ⓐ   Ⓑ

Figure 3. (A) Interaction diagram showing the frontier molecular orbitals of carbon dioxide and ethylene. (B) MO's resulting from the orbital interactions depicted in (A).

According to this generalized model, a cyclic array of six p atomic orbitals (AO's) can be topologically transformed into a homeomorphous array in which one center has two orthogonal p AO's, the remaining ones forming an angle of 45° with respect to the formers (Figure 5B). The resulting geometry has also no sign inversion and six electrons. Therefore, it is Hückel-aromatic and thermally allowed, similarly to the well-know aromatic array in the TS, of the Diels—Alder reaction (Figure 5A). According to this scheme, the thermal cycloreversion of 2-oxetanones can be alternatively viewed as a pericyclic or a coarctate[56] reaction.

Another interesting feature of **TSa** is the carbocation-like character of the C4 atom. Thus, the NBA charge of this atom at the HF/6-31+G* level is +0.580. The same analysis assigns a pure p localized orbital to this atom, with an occupancy of 0.399. The second-order perturbational analysis on the NBA basis reveals two stabilizing interactions involving the P_4^* orbital:

$\sigma^*_{2,3}$ P_4^* P_4^* LP_1

$\Delta E(2)$=-100 kcal/mol $\Delta E(2)$=-71.57 kcal/mol
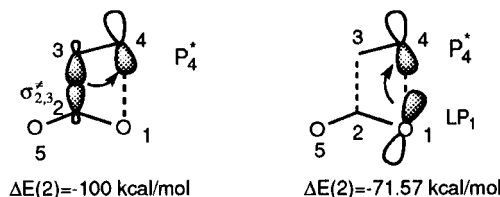
In addition, a lone pair of O1 also interacts with the π^* orbital between C2 and O5:

$\pi^*_{2,5}$ LP_1

$\Delta E(2)$=-156.17 kcal/mol

Therefore, the *supra—supra* interaction between **2a** and CO_2 can be described as a six-electron *retro* $[_\pi 2_s + (_\pi 2_s + _\omega 2_s)]$ process. In order to asses the possible biradical character of **TSa,** we

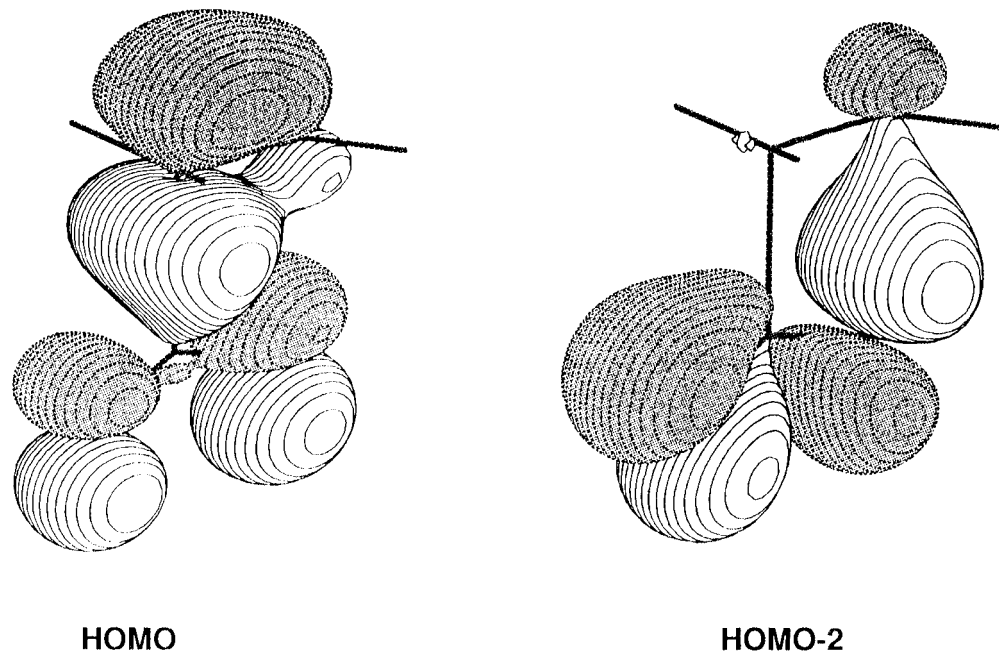**HOMO**   **HOMO-2**

Figure 4. Computer plot of the canonical HOMO and HOMO-2 of saddle point **TSa**, obtained at the HF/6-31+G* level.

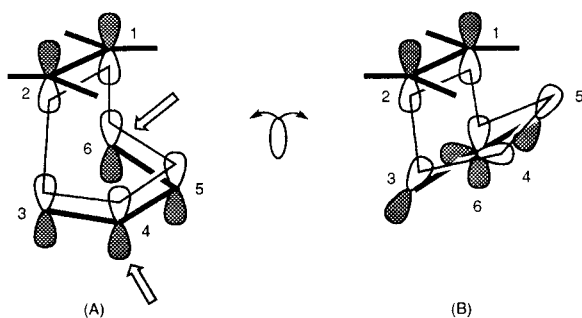**Figure 5.** Homeomorphous transformation of an aromatic Hückel ensemble of p-AO's associated to a [4+2] process into a [2+2] cycloaddition *via* constriction of the centers 4 and 6, as emphasized by the hollow arrows.

have performed a CASSCF(6,6)/6-31+G*//HF/6-31+G* calculation, including in the active space the orbitals resulting from the interactions depicted in Figure 3. We have found that, among the 175 configuration state functions (CSFs) generated, the CSF associated to the closed-shell S_0 wave function is largely the predominant one, with a coefficient of 0.974. In addition, the occupancies of the six natural orbitals included in the active window were found to be 1.968, 1.960, 1.978, 0.032, 0.022, and 0.040. Therefore, we concluded that the TS associated with the parent reaction has zwitterionic character and is described adequately with a single reference wave function.[57]

We have also calculated the reaction profiles of the thermal decarboxylation of 2-oxetanones depicted in Figure 1. The chief features of saddle points **TSb**−**j** are collected in Figure 6, and the corresponding energies of activation and reaction are shown in Table 2. As it can be seen, formation of allene **2b** *via* decarboxylation of 3-methylidene-2-oxetanone **1b** takes place with a higher activation barrier than that obtained for the parent reaction. This is due to severe distortion of the H_2C−C3−C4 bond angle at **TSb** with respect to that corresponding to **2b** (see Figure 6) and to the fact that the exocyclic π-system cannot provide additional stabilization to the electron-deficient C4 atom,

(57) Similar results have been found in previous computational studies on [2+2] cycloadditions. See refs 23b and 25. See also: Cossío, F. P.; Lecea, B.; Lopez, X.; Roa, G.; Arrieta, A.; Ugalde, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1450. For a related reaction involving a carboxylate anion, see: Antolovic, D.; Shiner, V. J.; Davidson, E. R. *J. Am. Chem. Soc.* **1988**, *110*, 1375.

since the involved orbitals are orthogonal each other. A similar result has been observed in the thermal cycloaddition between allene and isocyanic acid.[20]

The reaction of 3-methyl-2-oxetanone (**1c**) is very similar to the parent reaction from both geometrical and energetic standpoints (see Figure 6 and Table 2). However, a highly electronegative atom such as fluorine induces an enhancement in the activation energy. Thus, the **1d** → **2d** + CO_2 is predicted to take place with an activation barrier 1.83 kcal/mol and 1.23 kcal/mol higher than that computed for the parent reaction at MP2/6-31+G*//HF/6-31+G* and B3LYP/6-31+G* levels, respectively. This behavior is in agreement with the experimental evidence available,[8] and can be explained by the electron-withdrawing character of the fluorine atom. Thus, the energy associated with the two-electron $\sigma^{\neq}_{2,3} \rightarrow P_4^*$ interaction is 98.12 kcal/mol, 1.88 kcal/mol lower than the value found for the parent reaction (*vide supra*).

We have previously mentioned that the C4 atom in **TSa** is electron deficient in character. Therefore, it is expected that substitution at this atom by electron-releasing groups should stabilize the corresponding transition structures. This was found to be the case, and the result is again in agreement with the trends observed experimentally[1] (see entries 4−7 in Table 2). Thus, a hyperconjugative donor such as methyl induces a lowering in the activation energy of 3.8 kcal/mol with respect to the parent reaction at B3LYP/6-31+G* level (see Table 2, entry 4). An additional methyl group at C4 induces a lowering of 7.23 kcal/mol at the same level, thus suggesting that these effects are more or less additive (see Table 2, entry 5). As expected, strong π-donors which are able to delocalize a positive charge, such as vinyl or phenyl, induce even more pronounced energy lowerings and more asynchronous transition structures (see the main features of **TSg,h** in Figure 6). Thus, the energies of activation corresponding to the decarboxylation of **1g** and **1h** are found to be 9.02 kcal/mol and 10.03 kcal/mol lower, respectively, than that corresponding to the parent reaction (see the B3LYP/6-31+G* values of entries 6 and 7 in Table 2). 2-Oxetanones **1i,j** have been selected as model compounds to study the behavior of *cis* and *trans* stereomeric 2-oxetanones. As it can be seen from the data collected in entries 8 and 9 of Table 2, *cis*-3-methyl-4-vinyl-2-oxetanone (**1i**) is predicted to react slightly faster than its *trans* isomer **1j**, the differences in
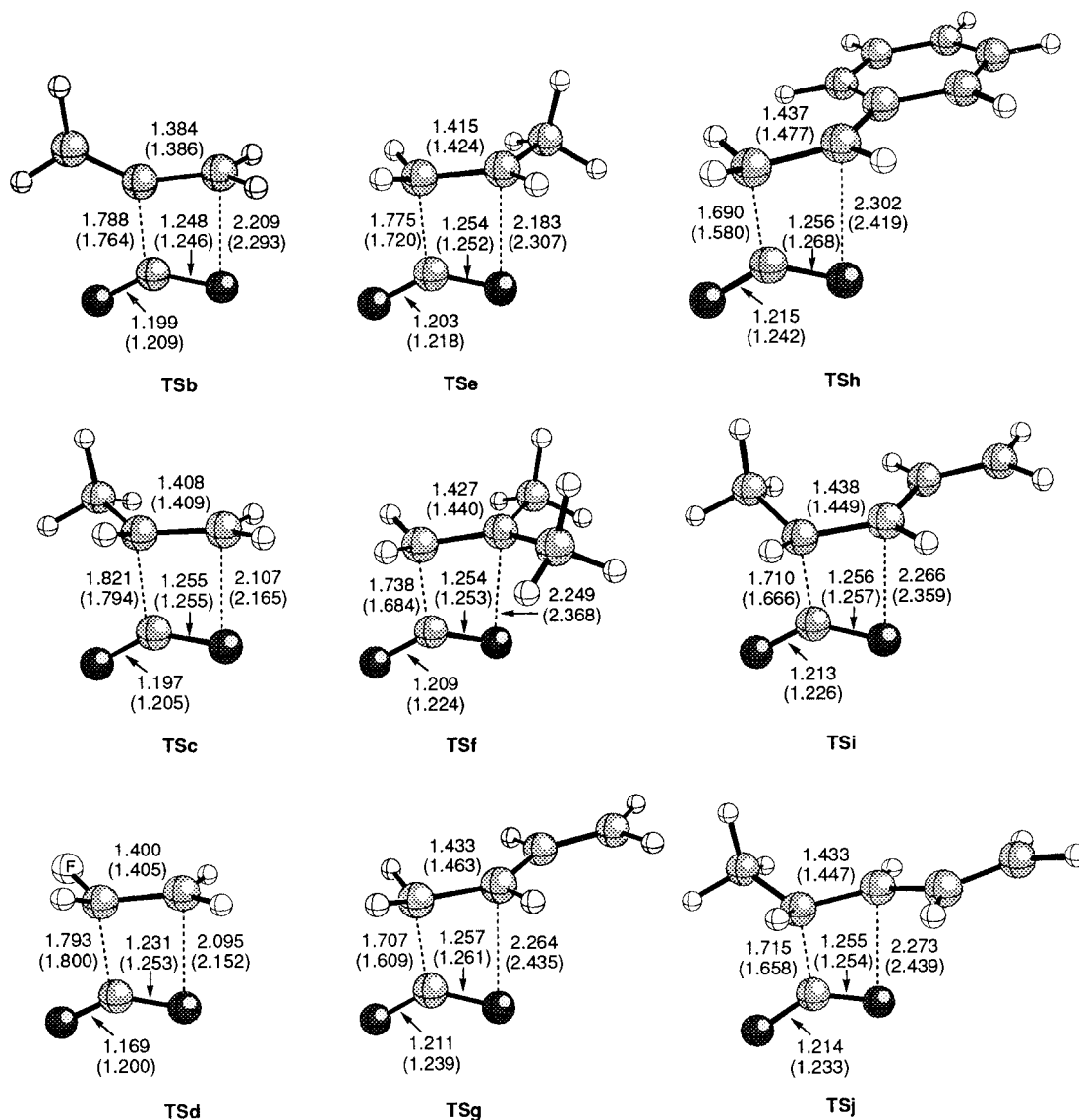
Figure 6. Ball-and-stick representations of transition structures **TSb−j** (see Figure 1), computed at the B3LYP/6-31+G* and B3LYP(L1A1)/6-31+G*, $\epsilon = 9.93$ (in parentheses). Bond distances are given in Å.

Table 2. Activation Energies,[a,b] (ΔE_a, kcal/mol), and Energies of Reaction,[a,b] (ΔE_{rxn}, kcal/mol) of the Thermal Decarboxylation of 2-Oxetanones **1b−j**

		ΔE_a		ΔE_{rxn}	
entry	substrate	MP2/ 6-31+G*	B3LYP/ 6-31+G*	MP2/ 6-31+G*	B3LYP/ 6-31+G*
1	**1b**	51.21(+9.24)	44.77(+7.84)	−8.11	−9.22
2	**1c**	41.81(−0.16)	37.11(+0.18)	−14.43	−16.29
3	**1d**	43.80(+1.83)	38.16(+1.23)	−21.29	−21.64
4	**1e**	39.97(−2.00)	33.13(−3.80)	−10.85	−12.93
5	**1f**	38.80(−3.17)	29.70(−7.23)	−7.82	−12.00
6	**1g**	36.90(−5.07)	27.91(−9.02)	−15.47	−18.27
7	**1h**	37.98(−3.99)	26.90(−10.03)	−13.08	−16.64
8	**1i**	36.98(−4.99)	28.29(−8.64)	−14.93	−19.48
9	**1j**	37.92(−4.05)	28.39(−8.54)	−15.60	−19.94

[a] The ZPVE corrections, computed at the HF/6-31+G* and B3LYP/6-31+G* levels, are included. [b] The MP2/6-31+G* values have been computed on fully optimized HF/6-31+G* geometries. [c] Values in parentheses are the relative activation energies with respect to the parent **1a → 2a** + CO$_2$ reaction.

Table 3. Activation Energies[a] (ΔE_a, kcal/mol) and Energies of Reaction[a] (ΔE_{rxn}, kcal/mol) of the Thermal Decarboxylation of 2-Oxetanone **1a**, Computed in *o*-Dichlorobenzene Solution ($\epsilon = 9.93$)

method	ΔE_a	ΔE_{rxn}
HF(L1A1)/6-31+G*	45.35	−16.74
MP2(L1A1)/6-31+G*//HF(L1A1)/6-31+G*	42.00	−10.81
B3LYP(L1A1)/6-31+G*	36.34	−11.14
HF(L6A3)/6-31+G*	42.03	−15.90
MP2(L6A3)/6-31+G*//HF(L6A3)/6-31+G*	41.89	−9.73
MP2(L6A3)/6-31+G*	40.89	−11.12
HF(PCM)/6-31+G*//HF/6-31+G*	48.48	−10.25
HF(IPCM)/6-31+G*//HF/6-31+G*	43.54	−17.50
HF(SCI-PCM)/6-31+G*	42.77	−17.62
MP2(SCI-PCM)/6-31+G*//HF(SCI-PCM)/6-31+G*	42.02	−7.40

[a] The ZPVE corrections, computed at the level of geometry optimization and conveniently scaled, have been included.

zene[29] solution. Therefore, this aspect of the reaction will be examined later (*vide infra*).

SCRF Results. As in the preceding section, we shall comment firstly the results obtained for the parent reaction in *o*-dichlorobenzene solution ($\epsilon = 9, 93$). The geometries of **TSa** in solution using different SCRF methods are depicted in Figure 2, and the corresponding energies are shown in Table 3. These data reveal that the activation energies do not vary significantly from one SCRF method to another. For example, the values
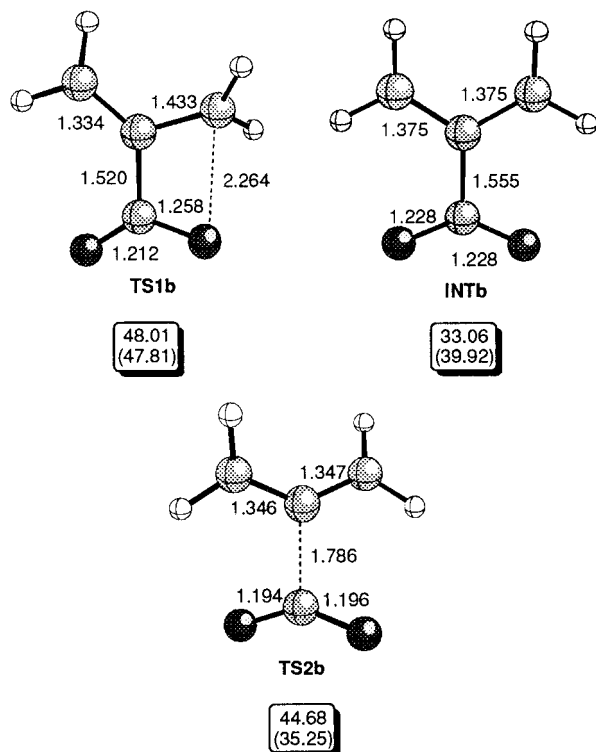
energy of activation being 0.94 kcal/mol and 0.10 kcal/mol at the MP2/6-31+G*//HF/6-31+G* and B3LYP/6-31+G* levels, respectively. This result is *not* in agreement with the experimental results, since the reverse relative reactivity has been observed.[26,29] However, it is noteworthy that these studies have been performed in decane or dodecane[26] and 1,2-dichloroben-

TS1b

48.01
(47.81)

INTb

33.06
(39.92)

TS2b

44.68
(35.25)

Figure 7. Stationary points found in the thermal decarboxylation of 3-methylidene-2-oxetanone **1b** at the HF(L1A1)/6-31+G* level. Bond distances are given in Å. Numbers in boxes correspond to relative energies in kcal/mol with respect to **1b**, computed at HF/(L1A1)/6-31+G*+ΔZPVE and MP2(L1A1)/6-31+G*//HF(L1A1)/6-31+G*+ΔZPVE (in parentheses) levels.

of ΔE_a for the parent reaction at the MP2/6-31+G*//HF/6-31+G* level using the L1A1, L6A3, and SCI-PCM approaches are 42.00, 41.89, and 42.02 kcal/mol, respectively. The PCM and IPCM values, computed on gas phase geometries, yield similar results. A relatively surprising result is that these values are very similar to those found in the gas phase. Since we have found that **TSa** has zwitterionic character, the charge separation should result in a significant stabilization of such a saddle point, thus lowering the activation energy. However, as it can be seen from the geometrical data reported in Figure 2, solvation promotes loss of synchronicity in **TSa**, and the bond distances between O1 and C4 are higher in solution (see Figure 2). In **TSa** the C_s symmetry is preserved in all the SCRF methods, with the only exception of L6A3. Thus, the values of the dihedral angle ω = O1−C2−C3−C4 are 26.9° and 25.4° at HF(L6A3)/6-31+G* and MP2(L6A3)/6-31+G* levels, respectively. In contrast, the L1A1 and SCI-PCM methods yield values of $\omega \approx 0.0°$. Since the PCM is equivalent to an infinite expansion of multipole terms, the former values are probably an artifact of the L6A3 method. In any case, from the topology of this saddle point (see Figure 5), it seems likely that the value of ω can vary at low energy cost, as it is reflected in the similar values of ΔE_a obtained using the L6A3 and the remaining SCRF methods.

The HF(L1A1)/6-31+G* potential energy surface of the reaction of 3-methylidene-2-oxetanone (**1b**) shows very significant differences with respect to the reaction profile found in the gas phase. Thus, we have located a first saddle point **TS1b** associated with the scission of the O1−C4 bond (see Figure 7). This TS lies 47.81 kcal/mol above **1b** at the MP2-(L1A1)/6-31+G*//HF(L1A1)/6-31+G*+ΔZPVE level. We have also located a zwitterionic intermediate **INTb** which lies 39.92 kcal/mol above **1b** at the same level. This intermediate seems quite plausible, since both the allyl cation and the carboxylate anion are quite stable ionic species. However, **INTb**

is planar and has C_{2v} symmetry (see Figure 7). Therefore, the chiral information contained in a substituted 3-alkylidene-2-oxetanone should be destroyed *via* zwitterionic intermediates such as **INTb**. This is not in agreement with the experimental evidence available, since it is known that decarboxylation of 3-alkylidene-2-oxetanones takes place with total stereocontrol to yield the corresponding allene with retention of configuration.[2a] The second transition structure **TS2b** (see Figure 7) associated with the cleavage of the C2−C3 bond has C_2 symmetry and lies 4.67 kcal/mol below **INTb** at the MP2(L1A1)/6-31+G*//HF(L1A1)/6-31+G*+ΔZPVE level. This result suggested that the stepwise mechanism could not be present at a correlated level. In effect, the potential energy surface of the **1b** → **2b** + CO_2 transformation at the B3LYP(L1A1)/6-31+G* level shows a concerted mechanism, and only **TSb** could be located, their geometric features being quite similar to those found in the gas phase (see Figure 6). This mechanism suggests total stereocontrol in the synthesis of allenes using this reaction.

Other 3-substituted-2-oxetanones such as **1c** and **1d** are predicted to be concerted both in the HF(L1A1)/6-31+G* and B3LYP(L1A1)/6-31+G* potential energy surfaces (see Table 4 and Figure 6). 4-Substituted-2-oxetanones incorporating methyl groups at C4 show a similar behavior. In all these cases, solvation induces a lowering in activation energy between 0.53 kcal/mol and 3.64 kcal/mol. This result is also in agreement with the experimental information available for the solvent effect in thermal decarboxylation of 2-oxetanones.[27] This energy lowering parallels an enhancement of the asynchronicity of these reactions, thus resulting in larger O1−C4 bond distances and lower C3−C4 bond distances (see Figure 6). In contrast, the ΔE_{rxn} values are lower in solution than in the gas phase, as it can be appreciated from the $\Delta\Delta E_{rxn}$ values in Table 4. This result is not surprising since 2-oxetanones are more polar than alkenes.

In the case of 4-vinyl-2-oxetanone (**1g**), the reaction is again predicted to be stepwise at both HF(L1A1)/6-31+G* and HF-(L6A3)/6-31G* levels (see Figure 8). It is interesting to note that the saddle point **TSRg** associated with the rotation around the C3−C4 bond is predicted to be of higher energy than **TS2g**, corresponding to the cleavage of the C2−C3 bond. Therefore, this stepwise mechanism is still compatible with the retention of configuration observed in the synthesis of enol ethers *via* thermolysis of *cis*- and *trans*-3-alkoxy (aryloxy)-2-oxetanones.[9] However, when the energies were recalculated at post-Hartree−Fock levels, the second saddle point **TS2g** was found to be lower in energy than **INTg**. Thus, at MP2(L1A1)/6-31+G* and MP2-(L6A3)/6-31G* levels, **TS2g** was 7.17 kcal/mol and 5.92 kcal/mol below **INTg**, respectively (see Figure 8). The same mutual relationship was found at higher levels. Thus, the values obtained at MP4SDTQ(L6A3)/6-31G* and QCISD(T)(L6A3)/6-31G* levels are 4.56 kcal/mol and 5.27 kcal/mol, respectively. Once again, the **1g** → **2g** + CO_2 transformation is predicted to be concerted at correlated levels. Thus, exploration of the B3LYP(L1A1)/6-31+G* energy hypersurface yields **TSg** as the only saddle point connecting reactant and products (see Figure 6). This transition structure is more asynchronous than its gas phase analogue, and the energy of activation in solution is again significantly lower than that found in the gas phase (see Table 4).

The same behavior is found in the SCRF study of the decarboxylation of 4-phenyl-2-oxetanone (**1b**). Thus, the reaction is predicted to be stepwise at the HF(L1A1)/6-31+G* level (see Figure 9 for the main geometric features of stationary points **TS1h**, **INTh**, and **TS2h**, as well as the relative energies with respect to **1h**). In this case, **TS2h** lies 5.68 kcal/mol below **INTh** at the MP2(L1A1)/6-31+G*//HF(L1A1)/6-31+G*+-

Table 4. Activation Energies[a] (ΔE_a, kcal/mol) and Energies of Reaction[a] (ΔE_{rxn}, kcal/mol) of the Thermal Decarboxylation of 2-Oxetanones **1a−j**, Computed in *o*-Dichlorobenzene Solution ($\epsilon = 9.93$)

substrate	MP2(L1A1)/6-31+G*[b]				B3LYP(L1A1)/6-31+G*			
	ΔE_a	$(\Delta\Delta E_a)^c$	ΔE_{rxn}	$(\Delta\Delta E_{rxn})^c$	ΔE_a	$(\Delta\Delta E_a)^d$	ΔE_{rxn}	$(\Delta\Delta E_{rxn})^d$
1a	42.00	(+0.03)	−10.81	(+3.46)	36.34	(−0.59)	−11.14	(+3.50)
1b	*e*	*e*	−3.63	(+4.48)	43.74	(−1.03)	−6.00	(+3.22)
1c	42.58	(+0.77)	−11.02	(+3.41)	36.58	(−0.53)	−13.47	(+2.82)
1d	44.61	(+0.81)	−18.53	(+2.76)	37.58	(−0.58)	−19.12	(+2.52)
1e	37.73	(−2.24)	−7.76	(+3.09)	30.55	(−2.58)	−9.20	(+3.73)
1f	32.81	(−5.99)	−4.95	(+2.87)	26.06	(−3.64)	−8.84	(+3.16)
1g	*e*	*e*	−12.51	(+2.96)	20.26	(−7.65)	−15.40	(+2.87)
1h	*e*	*e*	−11.43	(+1.65)	18.90	(−8.00)	−14.77	(+1.87)
1i	*e*	*e*	−12.89	(+2.04)	24.71	(−3.58)	−17.53	(+1.95)
1j	*e*	*e*	−12.79	(+2.81)	23.38	(−5.01)	−17.25	(+2.69)

[a] The ZPVE corrections, computed at the HF(L1A1)/6-31+G* and B3LYP(L1A1)/6-31+G* levels, are included. [b] Single-point relative energies computed on HF(L1A1)/6-31+G* geometries. [c] Relative values with respect to the MP2/6-31+G*//HF/6-31+G* results. [d] Relative values with respect to the B3LYP/6-31+G* results. [e] The HF(L1A1)/6-31+G* level predicts a stepwise mechanism (see text).

HF(L1A1)/6-31+G*
(MP2(L1A1)/6-31+G*)
HF(L6A3)/6-31G*
(MP2(L6A3)/6-31G*)

1.496
1.484
1.541
1.555
2.186
2.257
1.218
1.211
1.252
1.253
TS1g
24.64
(26.46)
27.18
(33.23)

1.485
1.447
1.562
1.635
1.239
1.220
1.230
1.222
INTg
18.32
(26.11)
23.31
(29.05)

1.483
1.487
1.577
1.594
1.225
1.238
1.237
1.222
TSRg
24.85
(30.62)
26.84
(35.47)

1.406
1.414
1.797
1.735
1.200
1.208
1.200
1.209
TS2g
23.46
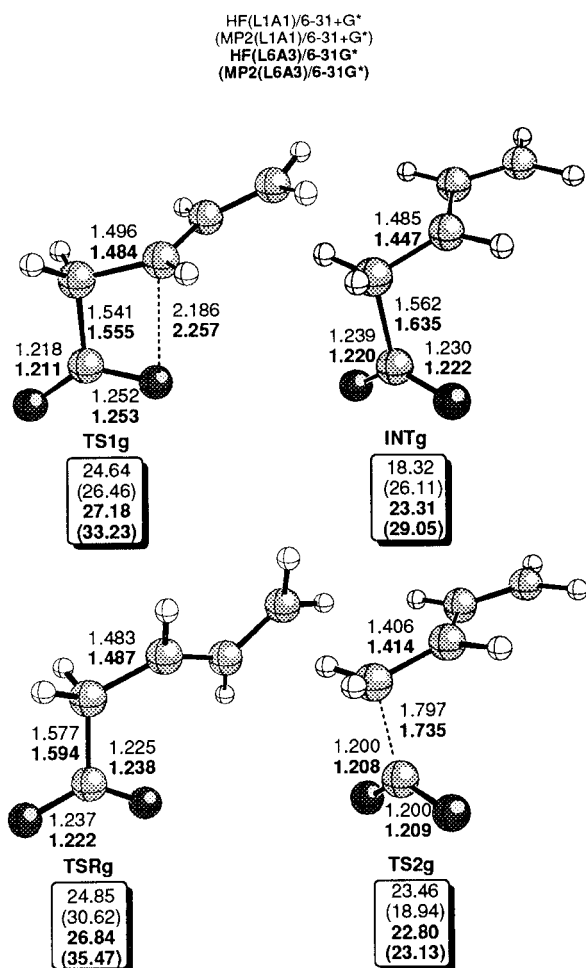(18.94)
22.80
(23.13)

Figure 8. Stationary points found in the thermal decarboxylation of 4-vinyl-2-oxetanone **1g** at the HF(L1A1)/6-31+G* and HF(L6A3)/6-31G* levels. Bond distances are given in Å. Numbers in boxes are the relative energies in kcal/mol with respect to **1g**, including ZPVE corrections. MP2 values are single point energies computed on the fully optimized HF geometries.

ΔZPVE level. The free energy difference between the same species computed at 140 °C is 5.37 kcal/mol, **INTh** being the less stable stationary point. As in the case of **1b** and **1g**, the reaction turns out to be concerted at the B3LYP(L1A1)/6-31+G* level, with an energy lowering in the activation energy of 8.00 kcal/mol with respect to the same value obtained in the gas phase. As it can be seen from the geometry of **TSh** at the B3LYP(L1A1)/6-31+G* level shown in Figure 6, this saddle point represents a limiting case between a concerted and a stepwise mechanism, the C2−C3 bond distance being very close

to (but slightly higher than) a standard C−C single bond. It seems likely that a more bulky substrate such as a *tert*-butyl group located at the C3 position (which is not tractable at this theoretical level with our computational resources) could yield a stepwise mechanism even at the B3LYP(L1A1)/6-31+G* level, thus permitting us to study the exceptional case reported by Mulzer in the thermolysis of *cis*- and *trans-tert*-butyl-4-phenyl-2-oxetanone in *o*-dichlorobenzene.[29]

From our results obtained at the HF(LnAm) level ($n = 1, 6$; $m = 1, 3$), it seems that the Hartree−Fock treatment tends to favor stepwise mechanisms in detriment of concerted ones. A possible explanation lies in the well-known fact that the HF level yields dipole moments which are 10−20% too large.[58] This overestimation of the dipole moment is amplified when the electrostatic part of the energy of solvation is evaluated. From eqs 5 and 6, the electrostatic component of free energy solvation is given by:

$$\Delta G_s = -\frac{\epsilon - 1}{2\epsilon + 1}\frac{\mu^2}{a_0{}^3} = \frac{1}{2}E_{int} \qquad (9)$$

This should result in a overestimation of the stability of highly polar zwitterionic species such as **INTb,g,h**, which incorporate highly stable cationic moieties such as allyl and benzyl cations, apart from the carboxylate anion. Given that correlated levels such as MP2 and B3LYP methods yield more realistic dipole moments,[58] the relative stabilities of stepwise and concerted mechanism are evaluated more accurately. We think that the above considerations can be extended to other reactions, and that care must be paid to processes in which solvent effects are investigated by means of SCRF methods based upon multipole expansions.

Finally, we have studied the decarboxylation of *cis*- and *trans*-3-methyl-2-oxetanones (**1i** and **1j**, respectively) in solution. Because of the reasons given above, the reaction profile of these reactions was found to be stepwise at the HF(L1A1)/6-31+G* level, the features of the corresponding stationary points being very similar to those found for **1g**. As expected, the B3LYP-(L1A1)/6-31+G* level yields concerted reaction pathways for both diastereomeric compounds. The important point, however, is that at this level the *trans* isomer **1j** is predicted to have an activation energy 1.33 kcal/mol lower than that of the *cis* isomer **1i** (see Table 4). This result is in agreement with the experimental work of Nishida[26] and Mulzer,[29] and corresponds to the opposite trend observed in the gas phase. According to our data, a concerted mechanism is compatible with a faster

(58) See, for example: (a) Sponer, J.; Leszczynski, J.; Hobza, P. *J. Phys. Chem.* **1996**, *100*, 1965. (b) Roa, G.; Ugalde J. M.; Cossío, F. P. *J. Phys. Chem.* **1996**, *100*, 9619.
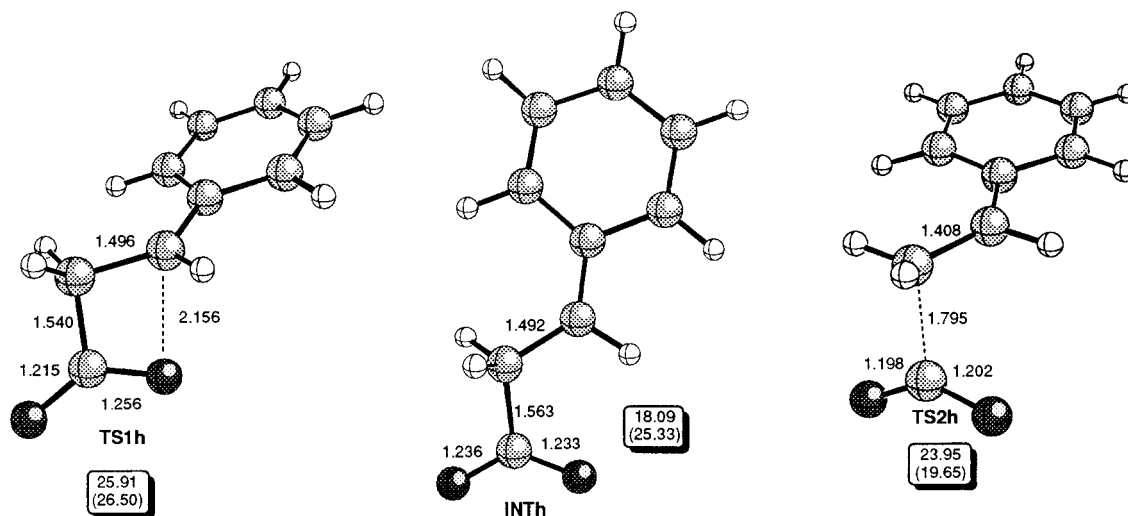
Figure 9. Stationary points found in the thermal decarboxylation of 4-phenyl-2-oxetanone **1h** at the HF(L1A1)/6-31+G* level. Bond distances are given in Å. Numbers in boxes correspond to relative energies in kcal/mol with respect to **1h**, computed at HF/(L1A1)/6-31+G*+ΔZPVE and MP2(L1A1)/6-31+G*//HF(L1A1)/6-31+G*+ΔZPVE (in parentheses) levels.

reaction for *trans*-2-oxetanones, provided that solvent effects are taken into account.

Conclusions

The mechanism of the thermal decarboxylation of 2-oxetanones to yield alkenes and carbon dioxide has been studied using *ab initio* methods and include solvent effects for the first time. The reaction is predicted to be concerted in the gas phase, and the saddle points connecting reactant and products have non-Woodward−Hoffmann topologies. This mechanism implies a suprafacial interaction for the alkene moiety. The C4 atom is electron deficient in the transition structure, and, therefore, donor substituents at this position induce a lowering in the activation energy. Given the polar character of these transition structures, the activation energies are in general lower in solution than in the gas phase. This effect is more pronounced when highly donating groups are present at the C4 position. SCRF methods based in the LnAm approach tend to overestimate the stability of zwitterionic intermediates at the HF level, thus predicting a loss of stereocontrol in the formation of olefins. This prediction is not in agreement with the experimental evidence, the only exception being 3-*tert*-butyl-

4-phenyl-2-oxetanone. Higher levels of theory predict that the reaction is concerted in solution, a 4-phenyl group representing the limiting case between a concerted and a stepwise mechanism. If solvent effects are taken into account, *trans*-2-oxetanones are predicted to react faster than their *cis* analogues.

Supporting Information Available: Tables of the total energies (in atomic units) of all stationary points discussed in the text (8 pages). See any current masthead page for ordering and Internet access instructions.

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