vessel thermostatted at 45.0 ± 0.1 °C. The resistance of the cell, measurable to ±1 Ω by means of a conductance system consisting of an oscilloscope and a AC Wheatstone bridge apparatus, was read every 2 min for fast reactions and every 15–30 min for slower ones for about 1 half-life; the second set of readings was taken at least 1 half-life later. Each rate constant is based on two to three sets of 10 or more resistance measurements. All were calculated by means of Guggenheim's method;[16] further details made be found in an earlier report from this laboratory.[23] The rate constants were fitted by means of the expression $\ln k = a + bP + cP^2$; b is then the slope $(\partial \ln k/\partial P)_T$ at $P = 0$, and ΔV_0^* follows as $\Delta V_0\sigma = -bRT$.[24] To assess interference from possible side reactions, control experiments were done with a 1.6 M solution of methyl iodide in acetonitrile alone. A conducting species does eventually form as indicated by a resistance drop into the measurable range (100 000 Ω); however, the interference had a negligible effect on the rate measurements.

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Registry No. **3**, 90554-37-3; **4**, 117860-46-5; **5**, 108-48-5; **6**, 110-86-1; **7**, 117860-47-6; **8**, 1149-23-1; 3,5-dibromopyridine, 625-92-3; 3,5-bis[2-(2-hydroxypropyl)]-2,6-lutidine, 117860-48-7; 3,5-diisopropenyl-2,6-dimethylpyridine, 117860-49-8; 3,5-bis(α-methylcyclopropyl)-2,6-dimethylpyridine, 117860-50-1; 3,3-dimethylbutanol, 624-95-3; 3,3-dimethylbutanal, 2987-16-8; 1-(3,3-dimethyl-1-butenyl)piperidine, 90554-29-3; *N*-*tert*-butylmethanimine, 13987-61-6; methyl iodide, 74-88-4; 3,5-di-*tert*-butylpyridine methiodide, 117860-51-2; 3,5-di-*tert*-butyl-2,6-dimethylpyridine methiodide, 117860-52-3; 2,6-lutidine methiodide, 2525-19-1; pyridine methiodide, 930-73-4.

Supplementary Material Available: Four tables of the rate constants referred to in this article (4 pages). Ordering information is given on any current masthead page.

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A Theoretical Study on the Mechanism of the Thermal and the Acid-Catalyzed Decarboxylation of 2-Oxetanones (β-Lactones)

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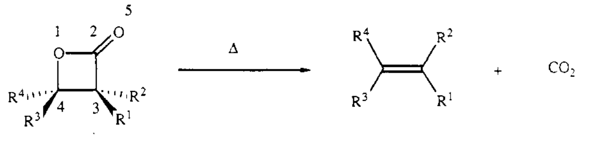
The thermolysis of 2-oxetanones (β-lactones) leading to carbon dioxide and olefins has been studied for the first time from the theoretical point of view by means of the semiempirical SCF-MO methods AM1, MNDO, and MINDO/3 at the RHF level. The reaction of the parent 2-oxetanone is predicted by all three methods to be concerted but highly asynchronous, taking place through a transition state with high zwitterionic character where all ring atoms lie in the same plane. An AM1-HE-CI study of the same process shows the absence of diradical character along the reaction path. The AM1 calculated enthalpy of activation and enthalpy of reaction are the closest to the experimental ones. The process has also been examined on a set of 25 diversely substituted 2-oxetanones by the AM1 method, the experimentally observed substituent effects being well reproduced by the calculations. The decarboxylation of 2-oxetanone protonated at the carbonyl oxygen atom has been studied as a model for the acid-catalyzed thermolysis of 2-oxetanones, finding that in this case the reaction takes place stepwise, through a carbocationic intermediate whose preferred conformation allows an interpretation of the observed stereochemical outcome of the reaction under acid catalysis. A reaction analysis by correlation of localized molecular orbitals has been performed on both the purely thermal and the acid-catalyzed processes, allowing the visualization of the electronic changes that take place along the reaction coordinate. Some simple ways of using the bond index concept for the study of chemical reactions are proposed. Application of these ideas to the thermolysis of 2-oxetanones reveals the existence of significant correlations between the parameters derived from bond index analysis and calculated enthalpies of activation.

Introduction

The thermal decarboxylation of β-lactones (2-oxetanones) is a well-established methodology for the stereospecific synthesis of subtituted olefins.[1] The reaction is also interesting from the mechanistic point of view, since it is one of the very few examples of a [2 + 2]-cycloreversion process taking place with retention of configuration (Scheme I).

Scheme I



On the other hand, the kinetics of the gas-phase thermal decomposition of the parent 2-oxetanone was studied several years ago,[2] and the process was found to be first order, the intermediacy of radicals being excluded by the fact that nitric oxide had no effect on the reaction rate.

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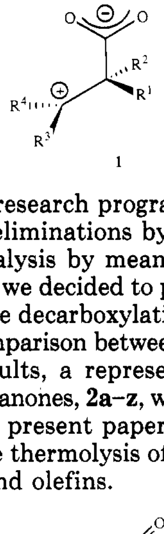
Further kinetic studies[3-8] have been performed in the past few years, mainly on aryl-substituted 2-oxetanones, but it is still not clear whether the reaction mechanism is a concerted one[3,4,7] or stepwise, proceeding through zwitterionic intermediate[5,6,8] **1**, which would preserve the relative stereochemistry at C_3 and C_4 by exhibiting a high rotation barrier around the C_3–C_4 bond due to the presence of through-bond and through-space 1,4-interactions. It is therefore surprising that up to now no attention has been paid to this subject from the theoretical point of view.



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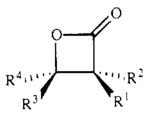
As a part of a research program devoted to the study of unimolecular eliminations by theoretical procedures, with reaction analysis by means of localized molecular orbitals (LMOs),[9] we decided to perform a comprehensive examination of the decarboxylation of 2-oxetanones **2**. In order to allow comparison between the theoretical and the experimental results, a representative set of diversely substituted 2-oxetanones, **2a–z**, was selected for this study. We report in the present paper the first theoretical investigation on the thermolysis of 2-oxetanones leading to carbon dioxide and olefins.



2a-z

Compound	R_1	R_2	R_3	R_4	Compound	R_1	R_2	R_3	R_4
2a	H	H	H	H	**2n**	H	H	OH	OH
2b	H	H	H	CH_3	**2o**	OH	H	OH	H
2c	CH_3	H	H	H	**2p**	OH	H	H	OH
2d	CH_3	CH_3	H	H	**2q**	OH	OH	OH	H
2e	H	H	CH_3	CH_3	**2r**	H	OH	OH	OH
2f	CH_3	H	CH_3	H	**2s**	H	H	H	C_2H_3
2g	CH_3	H	H	CH_3	**2t**	H	H	C_2H_3	C_2H_3
2h	CH_3	CH_3	CH_3	H	**2u**	H	H	H	C_2H
2i	H	CH_3	CH_3	CH_3	**2v**	H	H	C_2H	C_2H
2j	CH_3	CH_3	CH_3	CH_3	**2w**	H	H	H	C_6H_5
2k	H	H	H	OH	**2x**	H	H	C_6H_5	C_6H_5
2l	OH	H	H	H	**2y**	CH_3	H	C_6H_5	H
2m	OH	OH	H	H	**2z**	CH_3	H	H	C_6H_5

Theoretical Procedure

Due to the number and size of the molecular systems that are the subject of the present study, the calculations were performed with the AM1 method,[10] which appears to be the best available semiempirical procedure for the study of chemical reactions. For comparison, the decarboxylation of the unsubstituted 2-oxetanone **2a** was also studied with the MINDO/3[11] and MNDO[12] methodologies. The standard version of these methods was used as implemented in a locally modified version of the MOPAC package of programs,[13] which includes the AM1 hamiltonian. In order to test the existence of diradical character along the reaction path, the AM1 study on the thermolysis of **2a** was performed at both the RHF level and with a 3 × 3 configuration interaction (CI) based on molecular orbitals given by the "half-electron"[14] method (AM1-HE-CI), as suggested by Salem and Rowland for singlet states with diradical character.[15] Since the AM1-HE-CI calculated activation enthalpy for the thermolysis of **2a** turned out to be larger than the RHF one, the RHF version of AM1 was used for the study of the thermolysis of **2b–z**. As a further control test for diradical character, single point calculations were performed with the UHF formalism[16] (UAM1) on selected RHF calculated transition states, essentially zero expectation values for the $\langle S^2 \rangle$ operator and enthalpies of formation essentially equal to the RHF ones being recorded in all cases. Equilibrium geometries for reactants and products were determined by minimization of the energy with respect to all geometrical parameters using the DFP algorithm.[17] Initial attempts to locate the transition state (TS) for the thermolysis of **2a** along a minimum energy reaction path were unsuccessful, probably due to the complex nature of the reaction coordinate. This TS could be finally located by using the standard SADDLE[18] option implemented in MOPAC, which essentially consists of an interpolation between the structures of reactant and products. All other transition states in the present study were located starting from the optimized geometry of the TS in the thermolysis of **2a**, by pertinent substitution and optimization with the NLLSQ algorithm.[19] All transition states were refined by minimization of the gradient norm of the energy[20] and characterized by establishing that the Hessian (force constants) matrix had one and only one negative eigenvalue.[20] Attempts to locate hypothetical reaction intermediates on the potential energy hypersurface, in the neighborhood of the TS's, at either the RHF level (for **2a–z**) or the AM1-HE-CI one (for **2a**) proved unsuccesful. Allowance for geometrical relaxation from the TS's after small geometrical distortions led in all cases to the starting oxetanone and to the corresponding fragmentation products.

The localized molecular orbitals (LMOs) of reactants, products, and TS's were obtained with the localization procedure implemented in MOPAC, which essentially consists in a reformulation[21] of the Von Niessen density-localization criterion.[22]

The progress of the reactions was followed by means of the bond index (B_{xy})[23] between atoms x and y, as defined by eq 1, where $P_{\gamma\delta}$ are the elements of the density matrix

$$B_{xy} = \sum_{\gamma}\sum_{\delta} P_{\gamma\delta}^{2} \qquad (1)$$

and the subscripts γ and δ refer to atomic orbitals centered at atoms x and y, respectively.

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Whereas the geometrical analysis of the transition states is perhaps the most usual way to look at the results of theoretical studies on chemical reactions in terms of synchronicity/asynchronicity, and we have justified elsewhere[9] the advantages of the use of localized molecular orbitals (LMOs) for the same purpose in reactions taking place through closed shell species, providing a picture of the reactions in terms of the "movement" of bond orbitals and lone pairs which is closely related to the "curled arrow" representation familiar to organic chemists through the use of resonance theory, a comment should be made on the usefulness of bond indices for the study of the same kind of chemical reactions.

The bond index (B_{xy}) between two atoms x and y is a measure of the bond order and, hence, of the bond strength between these two atoms. Thus, if the evolution of the bond indices corresponding to the bonds being made or broken in a chemical reaction is analyzed along the reaction path, a very precise image of the timing and extent of the bond-breaking and the bond-making processes at every point can be achieved. It is worth noting that such an analysis is completely free of the subjective aspects associated to the geometric one, such as the estimation of the importance of bonding at distances considerably greater than the normal bond distance between two atoms (i.e., those existing in transition states) or the estimation of the evolution in bonding between two atoms when a small geometric change is associated to it (i.e., when a bond is just increasing or decreasing its order along a reaction). Moreover, assuming that the bond indices of the bonds not directly involved in a chemical reaction remain essentially constant as a whole along the reaction path (i.e., that the small individual changes cancel), an image of the overall bonding situation at every point of the reaction coordinate can be easily obtained.

In order to perform the bond index analysis, it is convenient to define a relative variation of bond index at the transition state (δB_i) for every bond (i) involved in a chemical reaction as

$$\delta B_i = (B_i^{\mathrm{TS}} - B_i^{\mathrm{R}})/(B_i^{\mathrm{P}} - B_i^{\mathrm{R}}) \qquad (2)$$

where the superscripts R, TS, and P refer to reactants, transition state, and products, respectively. Information from δB_i can be drawn in three different ways. First of all, their average value (δB_{av}) affords a measure of the degree of advancement of the transition state along the reaction path (i.e., the quantification of the "early" or "advanced" nature of a TS). Second, one can easily obtain information on the absolute asynchronicity (A) of a chemical reaction, defined as

$$A = 1/(2n - 2)\sum(|\delta B_i - \delta B_{\mathrm{av}}|/\delta B_{\mathrm{av}}) \qquad (3)$$

where n is the number of bonds directly involved in the reaction under consideration.[24] The A values obtained in this way are, in principle, independent of the degree of advancement of the transition state. It is important to realize that this precise definition of asynchronicity could be helpful in the clarification of the long lasting dispute on the synchronous or asynchronous nature of concerted reactions that are allowed in the Woodward–Hoffmann[25] sense, such as the Diels–Alder reaction,[26] the 1,3-dipolar cycloadditions,[27] and the Claisen[28] and Cope[29] [3,3]-sigmatropic rearrangements. Up to now, most discussions on this subject have been based on transition-states geometries, and we have already mentioned the limitations inherent to this approach. Bond index analysis could precisely show to what extent the results of the different theoretical treatments are in fact contradictory or not.

Table I. Relevant Geometrical Parameters[a,b] in the AM1 Optimized Transition States, Enthalpies of Activation[c] ($\Delta H^{\ddagger}$), and Enthalpies of Reaction[c] (ΔH_r) for the Thermal Decarboxylation of 2-Oxetanones 2a–z

compd	r_{12}	r_{23}	r_{34}	r_{41}	$\Delta H^{\ddagger}$	ΔH_r
2a	1.271	1.722	1.422	2.091	50.6	−9.2
2a[d]	1.262	1.712	1.435	2.158	78.6	+9.2
2a[e]	1.230	1.905	1.372	1.883	60.3	+9.4
2a[f]	1.272	1.849	1.414	1.949	50.9	−18.4
2b	1.275	1.636	1.444	2.181	43.1	−13.2
2c	1.270	1.765	1.427	2.053	50.5	−12.9
2d	1.270	1.857	1.431	1.972	50.3	−16.2
2e	1.280	1.592	1.478	2.215	36.2	−16.9
2f	1.274	1.653	1.450	2.168	43.1	−16.9
2g	1.273	1.656	1.449	2.171	43.7	−16.9
2h	1.272	1.678	1.445	2.158	43.6	−20.3
2i	1.278	1.608	1.475	2.212	36.5	−20.7
2j	1.276	1.626	1.481	2.208	36.6	−24.4
2k	1.277	1.600	1.468	2.211	35.0	−4.3
2l	1.270	2.011	1.434	1.841	51.9	−13.4
2m	1.264	2.065	1.433	1.837	51.4	−16.3
2n	1.289	1.568	1.497	2.155	24.6	−4.8
2o	1.264	1.648	1.486	2.248	38.4	−11.1
2p	1.264	1.639	1.485	2.249	35.8	−10.4
2q	1.257	1.648	1.498	2.302	40.2	−9.8
2r	1.266	1.604	1.511	2.265	22.5	−7.7
2s	1.275	1.616	1.453	2.212	41.2	−14.8
2t	1.279	1.602	1.462	2.231	37.9	−20.3
2u	1.274	1.638	1.447	2.186	42.7	−17.1
2v	1.276	1.600	1.471	2.238	35.6	−24.5
2w	1.276	1.608	1.456	2.217	39.9	−15.5
2x	1.281	1.573	1.483	2.241	33.8	−20.8
2y	1.274	1.626	1.460	2.206	42.3	−19.2
2z	1.274	1.625	1.461	2.213	40.7	−19.4

[a] Atom numbering as defined in Scheme I. [b] r_{xy} are the distances in angstroms between atoms x and y. [c] At 298 K, in kcal mol^{-1}. [d] MNDO results. [e] MINDO/3 results. [f] AM1-HE-CI results.

On the other hand, whereas the absolute asynchronicity of a chemical process could well be an intrinsic characteristic of multibond reactions,[27c] simply reflecting an energetic preference of the corresponding transition states over hypothetical, completely synchronous, ones, the relative asynchronicity of the bond-breaking and the bond-forming processes would be a measure of "bond defficiency" along the reaction path. Since the extent to which individual bonds are made or broken in the TS is

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(24) According to this definition, the asynchronicity of a concerted reaction where n is the total number of bonds broken and formed can vary between zero (when all of the n bonds have broken or formed at exactly the same extent in the TS) and one (when one of the n bonds has completely broken at the TS while the other ($n - 1$) bonds remain completely unchanged).

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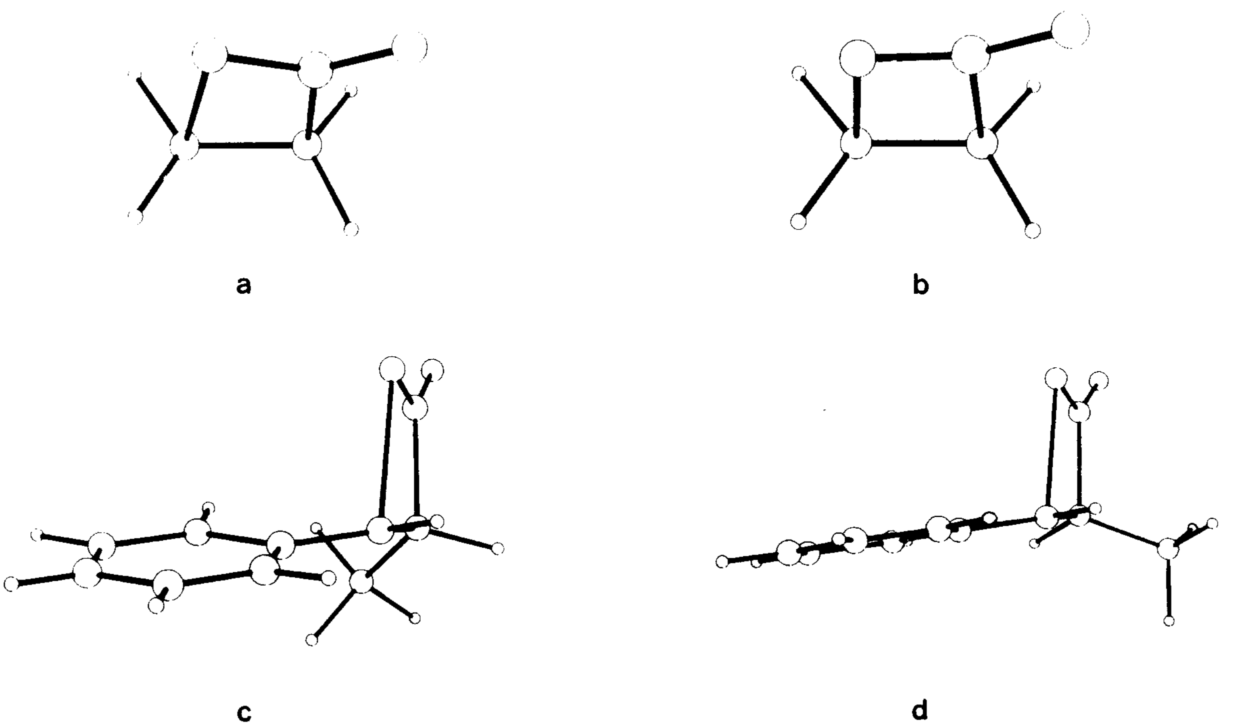

Figure 1. Computer plot of the calculated transition states for the thermal decarboxylation of (a) **2a** (AM1), (b) **2a** (MINDO/3), (c) **2y** (AM1), and (d) **2z** (AM1).

known from the calculation, a qualitative analysis of the activation enthalpy (ΔH^{*}) can be made in terms of bond components.

Results and Discussion

In all the studied cases, the thermal decarboxylation of β-lactones is predicted to be a concerted process taking place through a planar transition state with important zwitterionic character. The relevant geometrical parameters of the transition states for the decarboxylation of 2-oxetanones **2a–z**, together with the corresponding activation enthalpies, are summarized in Table I.

1. Thermolysis of 2-Oxetanone (2a). In the first place, in order to ascertain the relative merits of AM1, MNDO, and MINDO/3 in the description of the reaction, the decarboxylation of the unsubstituted 2-oxetanone (**2a**) was studied by all three methods at the RHF level.

Centering our attention on the geometric characteristics of the transition states (see the first three entries in Table I), the first important point to be noted is that AM1 and MNDO make a very similar asynchronous description of the reaction, with the O_1–C_4 bond essentially broken and the C_2–C_3 bond only slightly elongated with respect to its equilibrium distance in **2a** (AM1, 1.522 Å; MNDO, 1.538 Å). On the contrary, in the MINDO/3 calculated TS the O_1–C_4 and the C_2–C_3 distances have a very similar value, while O_1–C_2 and the C_3–C_4 are considerably shorter than in the corresponding AM1 and MNDO calculated transition structures (see Figure 1 for the most representative TS's in the thermal decarboxylation of 2-oxetanones **2a–z**). Thus, MINDO/3 describes the reaction as more synchronous and having a more advanced transition state.

The evolution of net charges on the ring atoms along the reaction path is summarized in Table II. As can be readily seen, all three methods describe the transition state as zwitterionic, with important net charges of opposite sign placed at O_1 and C_4.

A further aspect of the decarboxylation of **2a** where a comparison between the results of AM1, MNDO, and MINDO/3 should be made is the energetic one. Thus, if one compares the experimental values for the activation enthalpy (45.0 kcal mol^{-1})[2] and for the reaction enthalpy (−13.9 kcal mol^{-1})[23] with those predicted by the calculation (Table I), it is clear that AM1 gives the most accurate description of the reaction from the energetic point of view.

Table II. Evolution of Relevant Net Atomic Charges[a] along the Reaction Coordinate for the Thermal Decarboxylation of 2-Oxetanone According to AM1, (MNDO), and [MINDO/3]

reaction stage	q_1	q_2	q_3	q_4
2-oxetanone	−0.265	+0.300	−0.223	−0.041
	(−0.284)	(+0.314)	(−0.064)	(+0.122)
	[−0.490]	[+0.824]	[−0.170]	[+0.392]
transition state	−0.498	+0.450	−0.429	+0.241
	(−0.537)	(+0.455)	(−0.286)	(+0.421)
	[−0.638]	[+1.003]	[−0.291]	[+0.347]
CO_2 + ethylene	−0.206	+0.411	−0.218	−0.218
	(−0.224)	(+0.448)	(−0.080)	(−0.080)
	[−0.476]	[+0.952]	[−0.017]	[−0.017]

[a] Atom numbering, as defined in Scheme I for 2-oxetanone, is retained for transition state and products.

Since the zwitterionic character of the transition states for the decarboxylation could be in principle an artifact arising from the unsuitability of the RHF treatment for the description of conceivable diradical-like transition states, the thermolysis of **2a** was also studied with the AM1-HE-CI methodology,[14,15] as already mentioned.

Starting from the RHF optimized TS, a new transition structure could be located by minimization of the gradient norm of the energy[20] and characterized by diagonalizing the Hessian matrix[20] (ν_i = 1380 i cm^{-1}). Attempts to locate a diradical minimum on the HE-CI hypersurface were unsuccessful. The AM1-HE-CI calculated transition state turned out to be very similar from the geometrical point of view to the RHF one (see the fourth entry in Table I). In effect, the four-membered ring remains essentially planar and both the O_1–C_2 and the C_3–C_4 distances show values essentially coincident with those found in the RHF calculated TS. On the other hand, the C_2–C_3 distance is elongated by 0.127 Å whereas the O_1–C_4 one is shortened

Table III. Evolution of Relevant Bond Indices[a] along the Reaction Coordinate for the Thermal Decarboxylation of 2-Oxetanone[b] According to AM1, (MNDO), and [MINDO/3]

reaction stage	B_{12}	B_{23}	B_{34}	B_{41}
2-oxetanone	0.986	0.908	0.976	0.964
	(0.982)	(0.897)	(0.965)	(0.965)
	[0.899]	[0.887]	[0.969]	[0.920]
transition state	1.385	0.506	1.238	0.205
	(1.416)	(0.525)	(1.231)	(0.145)
	[1.371]	[0.254]	[1.514]	[0.145]
CO_2 + ethylene	1.891		2.002	
	(1.899)		(1.986)	
	[1.740]		[1.990]	
δB_i[a]	0.441	0.442	0.255	0.787
	(0.473)	(0.515)	(0.261)	(0.850)
	[0.561]	[0.714]	[0.534]	[0.842]

[a] According to eq 2. [b] Atom numbering, as defined in Scheme I for 2-oxetanones, is retained for transition states and products.

Table IV. Degree of Advancement of the Transition State (δB_{av})[a] and Absolute Asynchronicity (A)[b] in the Thermal Decarboxylation of 2-Oxetanone

	δB_{av}	A
AM1	0.481	0.211
MNDO	0.525	0.207
MINDO/3	0.663	0.116

[a] Mean value of δB_i in Table II. [b] According to eq 3.

by 0.142 Å. Accordingly, the AM1-HE-CI description of the thermal decarboxylation of **2a** is more synchronous with respect to the bond-breaking processes than the RHF one. It is interesting to note that, if diradical character had been present in the TS, the effect of CI inclusion in the calculation should have been the opposite one. Moreover, according to the CI matrix given by the calculation, the only configuration participating in the description of this species is essentially the closed shell-ground state one ($a^1b^1 = 0.1063$; $a^2 = 0.9923$; $b^2 = 0.0635$).

From the energetic point of view, the enthalpy of formation of the AM1-HE-CI calculated TS was 3.9 kcal·mol^{-1} *higher* than that of the RHF calculated one, and the enthalpy of formation of the starting 2-oxetanone was also 3.6 kcal mol^{-1} higher than the RHF value, so that the corresponding $\Delta H^{\ddagger}$ was 50.9 kcal·mol^{-1} (50.6 kcal·mol^{-1} for the RHF calculation). Furthermore, a single-point RHF calculation on the HE-CI optimized geometry led to a *decrease* of 3.0 kcal·mol^{-1} in the corresponding enthalpy of formation. These results clearly indicate that the transition state for the thermal decarboxylation of 2-oxetanone (**2a**) has no diradical character, since in other cases where diradical species are present along the reaction coordinate the HE-CI treatment gives lower activation energies than the RHF one.[26d,29c,30] The present theoretical result fully confirms the conclusions drawn from previous Hammett correlation studies,[4-6] which completely discarded the presence of diradicals or diradical-like TS's in the thermal decarboxylation of substituted 2-oxetanones.

With the validity of the RHF treatment for the thermolysis of 2-oxetanone (**2a**) secured by the results of the HE-CI study, the process was analyzed by correlation of localized molecular orbitals along the reaction path and by following the evolution of relevant bond indices along the reaction path.

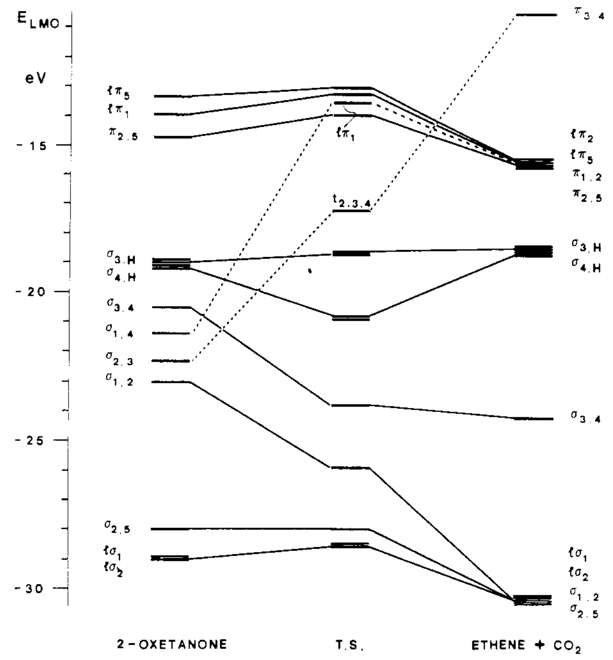

Figure 2. Correlation diagram of the localized molecular orbitals in the thermal decarboxylation of 2-oxetanone (**2a**). Atom numbering, as defined in Scheme I for the starting material, is retained for the transition state and products. The meaning of the labels is as follows: σ and π refer to the local symmetry of localized bicentric orbitals; l_σ and l_π refer to localized monocentric orbitals, and t refers to localized tricentric orbitals. The broken lines connect the orbitals corresponding to the bonds that are made or broken in the reaction.

The results of the bond index analysis of the reaction (Table III) fully confirm what was anticipated by inspection of the geometric characteristics of the TS's, as set up in Table IV.

Thus, according to AM1 and MNDO, approximately 80% of the initial C_4–O_1 bond and 50% of the initial C_2–C_3 bond have already vanished at the TS, whereas approximately 50% of the $\pi(O_1$–$C_2)$ bond and only 25% of the $\pi(C_3$–$C_4)$ bond have formed at this stage. In terms of bond index, both methods predict a transition state halfway between reactant and products ($\delta B_{av} \approx 50\%$), with an important asynchronicity in the reaction ($A \approx 21\%$). In the MINDO/3 calculation, by contrast, all of the bond-breaking and bond-forming processes are predicted to have taken place at a greater extent in the TS ($\delta B_{av} \approx 66\%$), the overall process being described as substantially more synchronous ($A \approx 12\%$). Finally, according to all three methods an important bond defficiency exists in the transition state (i.e., the bond-breaking processes are more advanced than the bond-forming ones), and this is translated into the important zwitterionic character reflected by the net atomic charges on the ring atoms (Table II).

In order to analyze the thermal decarboxylation of **2a** by correlation of localized molecular orbitals, the calculated LMOs for 2-oxetanone, transition state, and products were classified according to their local simmetry (σ or π) and nature (lone pair, bicentric or tricentric), and a correlation diagram was set up following the evolution of the LMOs from reactant to products through the transition state.[9] We will restrict the following discussion to the results of the AM1 study, but essentially the same applies for the correlation analysis of MNDO and MINDO/3 calculated LMOs. The correlation of the AM1 calculated LMOs is shown in Figure 2.

In this way, the movement of two electron pairs and the two-stage character of the reaction are easily visualized.

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(30) For semiempirical CI studies of reactions involving radical or biradicaloid TS's, see: (a) Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529. (b) Rayez, J. C.; Rayez, M. T.; Duguay, B. *J. Chem. Phys.* **1983**, *78*, 827. (c) Miller, L. S.; Grohmann, K.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 6862. (d) Dannenberg, J. J.; Tanaka, K. *J. Am. Chem. Soc.* **1985**, *107*, 671. (e) Dannenberg, J. J.; Rayez, J. C.; Rayez-Meaume, M. T.; Halvick, P. *J. Mol. Struct. THEOCHEM* **1985**, *123*, 343.

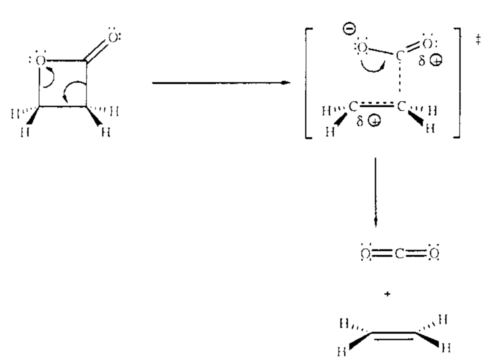

Figure 3. Schematic representation of the electronic reorganization along the reaction path in the thermal decarboxylation of 2-oxetanone.

In effect, in the first part of the reaction (from 2-oxetanone to the TS) the bond orbital between O_1 and C_4 ($\sigma_{1,4}$) is converted into a lone pair at O_1 ($1\pi_1$), and the electronic defficiency created at C_4 is partially compensated by the transformation of the C_2–C_3 σ bond ($\sigma_{2,3}$) of **2a** into a three-centered orbital delocalized between C_4, C_3, and C_2 ($t_{2,3,4}$). The carbocationic character of C_4 is also clearly shown by the substantial stabilization of the LMOs corresponding to the bonds that this atom forms with the adjacent hydrogens and with C_3. In the second part of the reaction coordinate, the lone pair at O_1 stabilizes by the formation of a π bond with C_2 (a π_{C-O} bond of carbon dioxide, $\pi_{1,2}$), while the delocalized orbital centered on C_4–C_3–C_2 smoothly rearranges to the ethylene π-bond ($\pi_{3,4}$). Putting all these facts together, the electron-pair description of the thermal decarboxylation of 2-oxetanone is schematically shown in Figure 3.

If we look now at the origin of the activation energy of this reaction, the LMO correlation analysis shows, as already indicated, that the $\sigma(O_1$–$C_4)$ bond orbital of 2-oxetanone is converted in the transition state into the 1_π orbital centered at O_1, which is the most destabilized during the course of the reaction. It is thus suggested that a substantial part of the activation energy of the process is due to the important breaking of the O_1–C_4 bond in the early stages of the reaction.

On the other hand, we have discussed the possibility of approximately partitioning the activation enthalpy of chemical reactions into bond terms by the use of the δB_i values. In the present case, inspection of Table III reveals a very important degree of breaking of the strong C_4–O_1 bond[31] in the TS, thus confirming the predictions of the LMO analysis. Also noticeable is the fact that the formation of the π bond between O_1 and C_2, although already advanced in the TS, has only a small stabilizing effect due to the very weak nature[31] of the π(C–O) bonds in CO_2.

In summary, both the correlation of LMOs and the bond index analysis of the reaction offer a coincident and satisfactory explanation for the origin of the activation enthalpy in the thermolysis of 2-oxetanone, the joint value of both methodologies being nicely demonstrated.

As a final comment on the suitability of AM1, MNDO, and MINDO/3 for the study of this particular process, all three methods appear to give a satisfactory description of the reaction. Since AM1 affords values of activation enthalpies and reaction enthalpies that are the closest to the experimental ones, we will restrict ourselves to AM1 calculations in the next sections of this discussion.

2. Substituent Effects in the Thermolysis of 2-Oxetanones. The effect of substituents on the course of the reaction is readily ascertained from inspection of Table I, and the observed trends are completely coincident with the description of the process that we have just discussed.

As it was logical to expect, substitution at C_4 by electron-releasing substituents always results in a substantial lowering of the activation energy of the reaction, the asynchronicity of the reaction being simultaneously enhanced. The predicted lowering in $\Delta H^\ddagger$ per methyl substituent at C_4 is about 7 kcal mol^{-1} [compare **2a** with **2b**, **2f**, **2g**, and **2h** (1 methyl group at C_4) and with **2e**, **2i**, and **2j** (2 methyl groups at C_4)]. Both ethynyl and vinyl substituents result in a larger (8–9 kcal mol^{-1}) decrease in $\Delta H^\ddagger$ (compare **2a** with **2s**, **2t**, **2u**, and **2v**), and the effect of phenyl substitution is still greater (10.7 kcal mol^{-1} lowering in **2w** and 16.8 kcal mol^{-1} in 4,4-diphenyl-2-oxetanone (**2x**)). As expected, the largest lowering is observed with the strong electron-donating hydroxy group [ca. 14 kcal mol^{-1} per hydroxy substituent at C_4, compare **2a** with **2k**, **2o**, **2p**, and **2q** (1 hydroxy group at C_4) and with **2n** and **2r** (2 hydroxy groups at C_4)].

On the other hand, the effect of substitution at C_3 is much less pronounced. From the energetic point of view, one or two methyl substituents at C_3 leave $\Delta H^\ddagger$ almost unaffected (compare **2a** with **2c** and **2d**, and **2b** with **2f**, **2g**, and **2h**), whereas the presence of hydroxy substituents at this position provokes a small increase of the activation energy (compare **2a** with **2l** and **2m**, and **2k** with **2o**, **2p**, and **2q**).

These calculated substituent effects are in complete accordance with the available experimental data; electron-donating aryl groups at C_4 strongly accelerate the thermal decarboxylation of 2-oxetanones,[3,4,6] while they have practically no influence on the reaction rate when located at C_3,[3] and the reaction is also accelerated when performed in solvents of increasing polarity,[6] what also agrees with the predicted zwitterionic nature of the TS's. Moreover, the predicted stabilizing effect of hydroxy substitution at C_3 in 2-oxetanones could explain the observed thermal stability of 4,4-dimethyl-3,3-diphenoxy-2-oxetanone, which sublimes on heating at atmospheric pressure without extensive decomposition.[1f]

Another aspect of the substituent effects in the thermolysis of 2-oxetanones that deserves comment is the variation of the synchronicity of the reaction. Inspection of Table I reveals that electron-donating substituents at C_4 tend to enhance the asynchronicity of the bond-breaking processes taking place in the reaction, whereas electron-donating substituents at C_3 have the opposite effect. Thus, in the TS's corresponding to the thermolyses of **2l** and **2m**, r_{23} is even greater than r_{41}, completely reversing what is observed with the parent **2a**.

As we have pointed out, bond index analysis can afford a deeper insight on the course of chemical reactions than the simple study of the geometrical characteristics of transition states. In order to apply such an analysis to the thermolysis of substituted 2-oxetanones **2b**–**z**, it was necessary to confirm first that no bonds other than those directly implied in the reaction suffered substantial changes in bond index along the reaction path. This turned out to be the case for all of the studied compounds except for the 4-hydroxy substituted ones **2k**, **2n**, **2o**, **2p**,

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[31] Assuming that bond dissociation energies could be appropriate references, the following estimation could be made for the strength of these bonds:

$$D_{\pi(O_1-C_2)} \approx D_{O{=}CO} - D_{CH_3O-COCH_3} = 31\ \text{kcal/mol}$$

$$D_{\sigma(C_4-O_1)} \approx D_{CH_3O-COCH_3} = 97\ \text{kcal/mol}$$

The *D* values have been taken from: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; p 146.

Table V. Relative Variation of Relevant Bond Indices in the Transition State (δB_i),[a,b] Degree of Advancement of the Transition State (δB_{av}), and Absolute Asynchronicity (A)[c] in the Thermolysis of Substituted[d] 2-Oxetanones

compd	δB_{12}	δB_{23}	δB_{34}	δB_{41}	δB_{av}	A
2a	0.441	0.443	0.256	0.787	0.482	0.211
2b	0.434	0.319	0.174	0.826	0.438	0.295
2c	0.443	0.466	0.258	0.765	0.481	0.197
2d	0.412	0.515	0.253	0.709	0.472	0.197
2e	0.409	0.227	0.100	0.825	0.390	0.388
2f	0.436	0.327	0.178	0.821	0.440	0.288
2g	0.439	0.330	0.178	0.826	0.443	0.288
2h	0.441	0.344	0.182	0.820	0.447	0.278
2i	0.419	0.239	0.106	0.830	0.398	0.379
2j	0.429	0.253	0.113	0.833	0.407	0.367
2l	0.381	0.612	0.251	0.613	0.464	0.213
2m	0.408	0.659	0.270	0.613	0.487	0.203
2s	0.448	0.282	0.148	0.838	0.429	0.333
2t	0.416	0.256	0.143	0.826	0.410	0.343
2u	0.448	0.326	0.179	0.822	0.444	0.287
2v	0.446	0.253	0.123	0.830	0.413	0.363
2w	0.450	0.265	0.135	0.836	0.422	0.350
2x	0.427	0.188	0.073	0.818	0.377	0.435
2y	0.453	0.256	0.145	0.836	0.422	0.351
2z	0.457	0.275	0.138	0.841	0.428	0.345

[a] Atom numbering as defined in Scheme I. [b] According to eq 2. [c] According to eq 3. [d] Compounds substituted at C_4 by hydroxy groups not included.

2q, and **2r**. In all these cases, the electronic defficiency created at C_4 by the breaking of the O_1–C_4 bond is compensated by formation of a partial π bond with the adjacent oxygen atoms of the hydroxy substituents rather than by the incipient formation of the $\pi(C_3$–$C_4)$ bond of the product olefin. Accordingly, the following bond index analysis will restrict to oxetanones bearing no hydroxy substituents at C_4. The relevant data are summarized in Table V.

Inspection of Tables I and V reveals some interesting trends. First of all, it is interesting to note that along the whole considered series the main sources of asynchronicity in the reaction are the great extent of the C_4–O_1 bond-breaking process and very incipient formation of the $\pi(C_2$–$C_3)$ bond in the corresponding TS's, in full accord with what is observed for the unsubstituted **2a**. Taking the decarboxylation of this compound as a reference, it can be seen that electron-donating substituents at C_4 exert a great influence on the course of the reactions, leading to earlier transition states (smaller δB_{av} values) with increased overall asynchronicity. By contrast, electron-donating substituents at C_3 exert, as anticipated from energetic considerations, very little effect on the reaction leading, in any case, to somewhat more advanced and more synchronous TS's. It is worth noting that the thermolyses of **2l** and **2m**, which could be considered as highly synchronous if only the bond-breaking processes were taken into account, turn out to take place with the same asynchronicity than the thermolysis of **2a** when all of the bond-breaking and the bond-forming processes are considered. In any case, the fact remains that these are the only two cases where the breaking of the C_2–C_3 and the O_1–C_4 bonds has proceeded in the TS to a comparable extent.

The observation of the evolution of ΔH^* with the corresponding values of A and δB suggested the existence of some kind of dependence between these parameters, and a least-squares analysis showed the existence of a very significant linear correlation between ΔH^* and A or δB (r = 0.97 in both cases). Plots of ΔH^* vs A and δB_{av} are shown in Figure 4. A corollary of the forementioned correlations is that A and δB_{av}, although independent by definition, are mutually correlated.

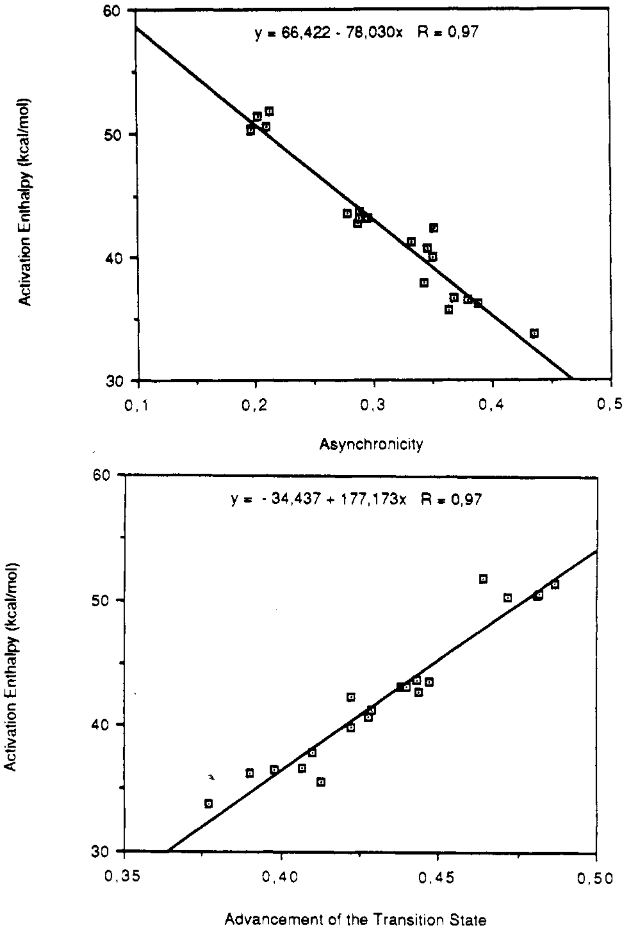

Figure 4. Linear correlation plots of (a) activation enthalpy vs absolute asynchronicity (A) (see eq 3) and of (b) activation enthalpy vs advancement of the transition state (δB_{av}) for substituted 2-oxetanones.

Some interesting consequences can be drawn from the mutual dependence of ΔH^*, A, and δB_{av}. In the first place, the variation of ΔH^* with δB_{av} represents a verification and a quantification of the Hammond postulate[32] within the context of this particular reaction. Thus, given a reference TS, structural changes in the reactant leading to earlier TS's involve a parallel decrease in the activation energy of the process. Secondly, the variation of ΔH^* with A has to be ascribed to the fact that a concerted and completely synchronous $[2\pi_s + 2\pi_s]$ cycloreversion[33] would be forbidden in the Woodward–Hoffmann sense. The more asynchronous the reaction, the lower its activation energy is. It thus appears that asynchronicity is the means by which the thermal decarboxylation of 2-oxetanones avoids the "forbidden" character of the hypothetical completely synchronous process.

Of course, all the preceding considerations apply only to situations where the bond index analysis can be properly performed, i.e., when only the bond indices corresponding to the bonds directly involved in the reaction experiment a substantial change along the reaction path. For instance, application of the same bond index analysis to the thermolysis of the 4-hydroxy-substituted 2-oxetanones would lead to mistified values of A and δB_{av}, since the formation of partial $\pi(C$–$O)$ bonds between C_4 and the adjacent oxygen atoms in the substituent hydroxy groups would not

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(32) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(33) Both the planar geometries predicted for the transition states and the LMO analysis of the reaction clearly indicate the supra–supra nature of the reaction.

be taken into account. By contrast, the derived stabilization of the TS would be reflected in the calculated $\Delta H^{\ddagger}$ value. It is to be mentioned that this kind of stabilization points out the way by which a transition state can become an intermediate in a limit situation, thus provoking a mechanistic change in the reaction.

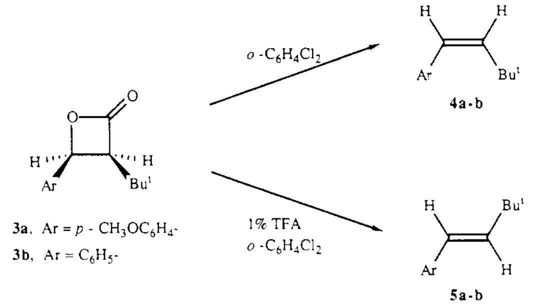
3. Cis/Trans Effect. An intriguing experimental observation on the thermal decarboxylation of 3-alkyl-4-aryl-2-oxetanones is the fact that the trans isomer reacts more rapidly than the corresponding cis isomer without exception.[5,7] This fact has been diversely interpreted, either as proving the existence of a discrete zwitterionic intermediate[5] or as showing that the reaction is concerted and transcurs via a $[2\pi_s + 2\pi_a]$ transition state.[7]

In order to clarify this point, we have studied the decarboxylation of *cis*- and *trans*-3-methyl-4-phenyl-2-oxetanone (**2y** and **2z**). The experimentally found[7] difference in activation enthalpy for the thermolysis of these compounds is 2.9 kcal mol^{-1} in favor of the trans isomer ($\Delta H^{\ddagger}_{cis}$ = 32.3 kcal mol^{-1}; $\Delta H^{\ddagger}_{trans}$ = 29.4 kcal mol^{-1}). Since AM1 predicts for this pair of compounds (see Table I) a difference in $\Delta H^{\ddagger}$ of 1.6 kcal mol^{-1} in the same direction, it can be concluded that the concerted mechanism taking place through a zwitterionic TS predicted by AM1 for this reaction can cope with the experimental results, without any need to resort to alternative mechanisms. A more interesting question is about the reason why this fact occurs and how it is explained by the calculation. Looking at the results of the theoretical study, AM1 predicts that the trans oxetanone (**2z**) is 1.4 kcal mol^{-1} more stable than the cis one (**2y**). In the corresponding TS's, the difference in ΔH_f has raised up to 3.0 kcal mol^{-1}. If one looks at the geometrical characteristics (Table I) or to the bonding situation (Table V) of both transition states, no significant differences can be appreciated. The only important remaining fact that could exert a differential stabilizing effect on the starting 2-oxetanones and the zwitterionic transition states is a conjugative interaction with the substituent phenyl group at C_4. We have represented in Figure 1 the calculated TS's for the thermolyses of **2y** and **2z**. As can be seen, in the TS corresponding to the thermal decarboxylation of the trans isomer the phenyl group lies on a plane that is almost completely perpendicular to that of the lactone ring, thus allowing a conjugative interaction between the carbocationic-like C_4 atom and the phenyl substituent. By contrast, in the TS corresponding to the cis isomer **2y**, the phenyl group has tilted 18° out of this plane in order to minimize the steric repulsions with the adjacent *cis*-methyl substituent. It is logical to expect that any conjugative interaction that could stabilize the trans TS will be diminished in the cis one. According to that, the ultimate reason why *trans*-4-aryl-3-alkyl-2-oxetanones decarboxylate faster than the corresponding cis isomers would simply be the greater stabilization of the trans zwitterionic transition states through a repulsion-free conjugative interaction with the substituent phenyl group.

4. Acid-Catalyzed Thermolysis of 2-Oxetanones. In 1981, Mulzer and Zippel[8] reported that, increasing the acidity of the reaction medium, the stereochemistry of the decarboxylation of *cis*-3-*tert*-butyl-4-aryl-2-oxetanones **3a** and **3b** gradually changed from total retention to total inversion of configuration, while the reaction rate was greatly increased in a simultaneous manner (Scheme II).

Thus, when the thermolysis of **3a** was performed in *o*-dichlorobenzene at 100 °C, the *Z* olefin **4a** was obtained in more than 98% stereochemical purity, and changing the solvent to 1% trifluoroacetic acid/*o*-dichlorobenzene, the *E* olefin **5a** was obtained, also with more than 98% stereochemical purity, the reaction rate being increased by a factor of 15000 (by extrapolation to 100 °C).

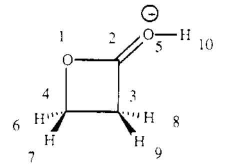
Scheme II



An explanation for these facts was offered in the context of the proposed stepwise mechanism for the purely thermal reaction, by assuming that the protonation of the zwitterionic intermediate **1** (which, as it has already been mentioned, should exhibit a sizable barrier to rotation because of 1,4-interactions) had the double effect of stabilizing the negative charge of the carboxylate moiety and suppressing the 1,4-interactions. The possibility of fast rotation around the C_3–C_4 bond could then lead to the exclusive formation of the thermodinamically more stable olefins **5a** and **5b**.

However, as we have shown in the preceding sections, the present calculations, while accounting for all known experimental facts about the purely thermal decarboxylation of 2-oxetanones, indicate that the hypothetical zwitterionic intermediate **1** is never present along the reaction coordinate, the reaction being concerted and taking place in all cases through an essentially planar TS. It is worth noting that this stands also for the thermolysis of **2y**, which is closely related to **3a** and **3b**.

In order to ascertain whether the AM1 calculations were also able to account for the forementioned experimental facts, we have studied the decarboxylation of 2-oxetanone protonated at the carbonyl oxygen (**6**), taken as a model for the acid-catalyzed reaction.



6

The located stationary points and the calculated energy profile for the reaction are represented in Figure 5 and the relevant information on geometrical parameters, bond indices, and enthalpies of formation is summarized in Table VI.

As can be seen, the decarboxylation of carbonyl-protonated 2-oxetanone **6** is no longer a concerted reaction and involves (in the gas phase) two distinct intermediates. In the first part of the reaction coordinate, which leads to the first transition state **7** with an enthalpy of activation of 17.7 kcal mol^{-1}, takes place the breaking of the O_1–C_4 bond. The geometrical and bonding characteristics of **7** are very similar to those of the TS in the concerted reaction, but now the process becomes almost completely asynchronous, and the C_2–C_3 bond is not appreciably broken in **7**. This is clearly shown in the simplified LMO correlation diagram represented in Figure 6.

While the σ-bond orbital C_2–C_3 remains essentially unaffected on going from **6** to **7**, the original σ–bond orbital O_1–C_4 of **6** is strongly destabilized in **7** by conversion into a π lone pair centered at O_1. This TS relaxes to the rel-

Table VI. Relevant Geometrical Parameters,[a,b] Bond Indices,[a] and Enthalpies of Formation[c] for the Stationary Points in the Decarboxylation of Protonated 2-Oxetanone

structure	r_{12}	r_{23}	r_{34}	r_{41}	Φ^d	B_{12}	B_{23}	B_{34}	B_{41}	ΔH_f
6	1.341	1.513	1.561	1.527	109.3	1.298	0.939	0.969	0.872	127.2
7	1.254	1.509	1.490	2.268	90.1	1.658	0.909	1.016	0.154	144.9
8	1.229	1.508	1.423	2.827	0.0	1.820	0.905	1.239	0.007	133.9
9	1.179	2.196	1.364	2.837	91.3	2.114	0.240	1.601	0.078	155.4
10	1.178	2.251	1.363	2.887	92.4	2.119	0.214	1.610	0.079	155.4
11	1.155					2.369				147.8
ethylene			1.326					2.002		16.5

[a] Atom numbering as defined in structure **6**. [b] r_{xy} are the distances in angstroms between atoms x and y. [c] At 298 K, in kcal/mol. [d] Φ is the absolute value in degrees of the dihedral angle between the bonds C_2–C_3 and C_4–H_6.

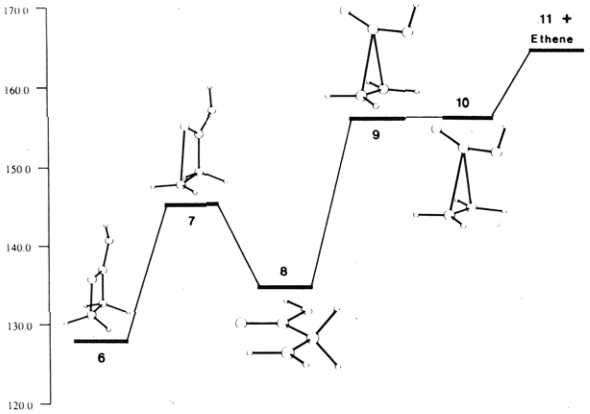
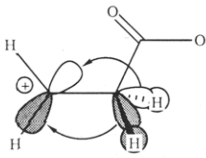


Figure 5. Calculated energy profile and computer plot of stationary points in the reaction coordinate of the thermal decarboxylatin of protonated 2-oxetanone **6** (AM1).

atively stable intermediate **8** with important geometrical changes. The most important geometric feature of this intermediate (see Figure 5 and the value of the dihedral angle Φ in Table VI) is the rotation around the C_3–C_4 bond, which results in a bisected conformation for the ethylene moiety of the molecule. This important conformational change takes place in order to allow the stabilization of the positive charge at C_4 by hyperconjugation with the C_3–H_8 and C_3–H_9 bond orbitals.



8

This hyperconjugative stabilization is clearly seen by comparing the LMOs corresponding to the C_3–H bonds in **7** and **8**. While they are almost completely bicentric in **7** (59.3% located at C_3 and 39.2% at one of the hydrogen atoms), they become appreciably delocalized over C_4 in **8** (57.5% located at C_3, 35.9% at one of the hydrogen atoms, and 5.9% at C_4). From this intermediate, the reaction continues by the breaking of the C_2–C_3 bond, which takes place simultaneously with the stabilization of the π lone pair at O_1 by conversion into the O_1–C_2 π-bond of protonated carbon dioxide **11**. A rotation around the C_3–C_4 bond takes place again, leading to an eclipsed conformation in order to allow the smooth conversion of the C_2–C_3 σ-bond into the C_3–C_4 π-bond of the olefin. This process takes place with an activation energy of 21.6 kcal mol^{-1} and leads to the symmetric intermediate **10**, which lies less than 0.1 kcal mol^{-1} below the preceding TS, **9**. Due to the geometrical features of **9**, where the O_1, C_2, and O_5 atoms lie in a plane that is perpendicular to the C_3–C_4 bond (see Figure 5), it could be thought that this intermediate indicates a supra–antara approach for the addition of protonated carbon dioxide to ethylene. That this is not the case is shown by the low value of the O_1–C_4 bond index in both **9** and **10** (see Table VI). In fact, **10** is a true π complex between ethylene and the strongly electrophilic **11**, as demonstrated by the existence in its set of LMOs of a tricentric orbital embracing C_2, C_3, and C_4 (see Figure 6), which is built almost exclusively from an sp^3 hybrid centered at C_2 interacting in a cyclic way with the p_z orbitals at C_3 and C_4.

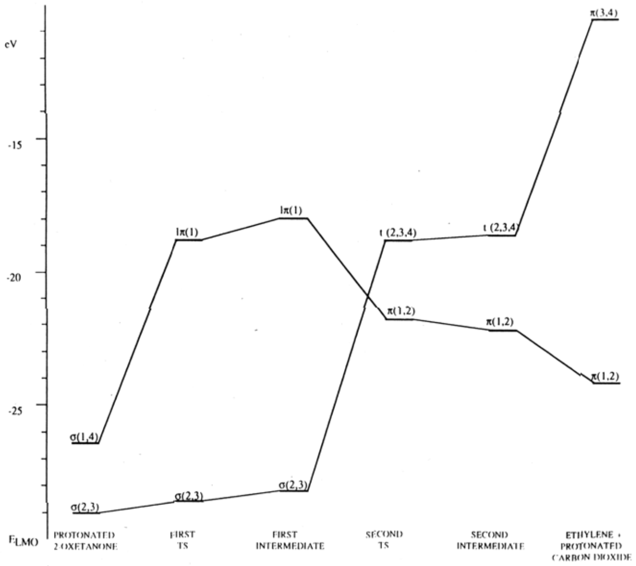
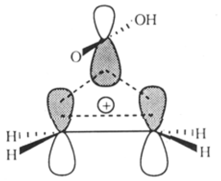


Figure 6. Correlation diagram of the localized molecular orbitals corresponding to the two breaking bonds in the decarboxylation of protonated 2-oxetanone **6**. For the meaning of the labels, see Figure 2.



10

According to the present results, which refer to gas phase, the π complex **10** would arise in a synthetic sense from an interaction between ethylene and protonated carbon dioxide **11** without energetic barrier, i.e., as both components separate the enthalpy of formation of the supermolecule approaches to the sum of ΔH_fs of **11** and ethylene.

It can be readily seen that the mechanism we have just discussed accounts for the known experimental facts on the acid-catalyzed decarboxylation of 2-oxetanones. In the first place, the calculated overall reaction barrier is 37.1 kcal mol^{-1} (13.5 kcal mol^{-1} lower than the activation energy of the purely thermal concerted process), so that the strong acceleration observed[8] is readily explained. On the other hand, the rotation around the C_3–C_4 bond, which occurs as the stable intermediate **8** forms, nicely explains the inversion of configuration observed by Mulzer and Zippel in the acid-catalyzed decarboxylation of the sterically congested *cis*-3-*tert*-butyl-4-aryl-2-oxetanones **3**.[8] In effect, since an intermediate similar to **8** (on which the substituent at C_4 would take the place of the hydrogen atom in the less hindered conformation) can lead either to the *Z* or to the *E* olefin simply by rotation around the C_3–C_4 bond in one or other direction, it is clear that the different thermodynamic stabilities of the olefins (or, what is equivalent, of the π complexes like **10** leading to them) will result in the formation of (*E*)-alkenes **5**, irrespectively of the cis or trans configuration of the starting oxetanone.

Conclusions

The following conclusions can be drawn from the present study: (1) The semiempirical SCF MO methods AM1, MNDO, and MINDO/3 at the RHF level predict that the thermal decarboxylation of 2-oxetanone is a concerted yet asynchronous process taking place through a planar transition state with high zwitterionic character. The AM1 calculated enthalpy of activation and enthalpy of reaction are the closest to the experimental values. (2) According to AM1 results on the thermolysis of a series of diversely substituted 2-oxetanones, the presence of electron-donating substituents at either C_3 or C_4 does not modify the concerted character of the reaction. In any case, the presence of such substituents at C_4 provokes an important increase in the asynchronous character of the reactions, together with a significant decrease in their enthalpies of activation, while the same substituents at C_3 exert a much less important effect in the opposite direction. These predictions are in full agreement with experimental observations. (3) The AM1 results on the thermal decarboxylation on *cis*- and *trans*-3-methyl-4-phenyl-2-oxetanone predict that the trans compound will decarboxylate more rapidly than the cis one and offer an explanation for this behavior on the basis of a differential stabilization of the corresponding transition states through conjugation of the electron-deficient C_4 atom with the phenyl substituent. This allows a satisfactory explanation of what is observed in the thermolysis of *cis*- and *trans*-3-alkyl-4-aryl-2-oxetanones without need to resort to a change in the mechanism of the reaction. (4) The AM1 results on the thermal decarboxylation of 2-oxetanone protonated at the carbonyl oxygen atom indicate that the process takes place stepwise, through a bisected carbocationic intermediate stabilized by hyperconjugation, and with an activation enthalpy much lower than the purely thermal concerted process. This result gives a theoretical explanation to the experimental fact that the acid-catalyzed decarboxylation of 3-*tert*-butyl-4-aryl-2-oxetanones is much faster than the purely thermal process and that, whereas under neutral conditions the process shows syn stereospecificity, in the acid-catalyzed reaction the more thermodynamically stable *E* olefin is obtained with high stereoselectivity.

In summary, the results of the present calculations account for all of the known experimental facts regarding the thermal decarboxylation of β-lactones, affording a complete mechanistic picture of this synthetically useful reaction. It is worth noting here that the possibility for concerted $[2\pi_s + 2\pi_s]$ character in the extrusion of carbon dioxide from 2-oxetanones was pointed out several years ago by Epiotis[34] on the basis of qualitative MO considerations.

From a methodological point of view, we have applied to the study of the reaction the correlation of localized molecular orbitals,[9] allowing the description of the process in terms of the movement of electron pairs, and we have proposed some simple ways for using bond indices[23] in the study of chemical reactions. The bond index analysis can be properly applied to chemical reactions taking place through closed-shell species where only the bonds directly involved in the chemical process under consideration suffer substantial changes along the reaction path and allows a quantification of commonly employed (but loosely defined) concepts such as advancement of the transition state or asynchronicity of chemical reactions. When these ideas have been applied to the reaction under consideration, a very good agreement with the LMO analysis of the activation enthalpy has been found, as well as the existence of very significant correlations between the parameters derived from the bond index analysis and the calculated enthalpies of activation for the thermal decarboxylation of substituted 2-oxetanones.

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Supplementary Material Available: Cartesian coordinates of the optimized molecular structures (45 pages). Ordering information is given on any current masthead page.

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