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THE ELECTRONIC STRUCTURE OF β-PROPIOLACTONE (2-OXETANONE) AND OF SOME 3- AND 4-SUBSTITUTED 2-OXETANONES

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ABSTRACT

STO-3G calculations were performed on several 4-substituted 2-oxetanones (β-lactones), with the aim of rationalizing their very different chemical stabilities. A direct correlation was found between the relative thermal stabilities of the substituted β-lactones and the respective energies of their HOMO and LUMO.

INTRODUCTION

Widely used in synthetic [1] and in polymer [2] chemistry, 2-oxetanones (β-lactones), Fig. 1, are quite versatile molecules. Their reactivity is largely associated with ring strain and, depending upon experimental conditions, ring opening occurs with C—alkyl—oxygen or C—acyl—oxygen bond breaking [3]. However, not much has been reported on the thermal stability of β-lactones, which is very sensitive to ring substitution where the position and nature (e.g., saturation or unsaturation) of substituents are of foremost importance. For example, 4-propenyl-2-oxetanone, referred to as g in Table 1,
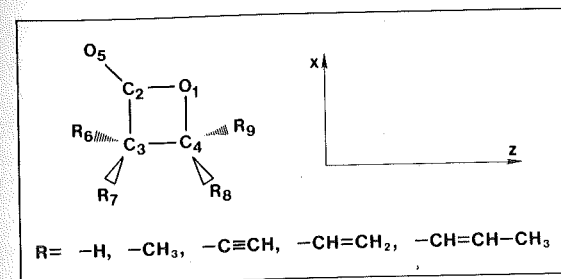

Fig. 1. Geometry of the four-membered ring in 2-oxetanone, the numbering of the atomic sites is as used throughout the paper, and the orientation of the molecular framework is in the Cartesian reference system.
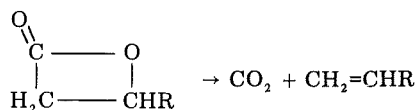
TABLE 1

List of the 3- and 4- substituted-2-oxetanones studied in this work

Identification code	Substitution site*	Substituent	Compound
a	—	—H	2-oxetanone
b	4	—CH₃	4-methyl-2-oxetanone
c	3	—CH₃	3-methyl-2-oxetanone
d	3,3	—CH₃	3,3-dimethyl-2-oxetanone
e	4	—C≡CH	4-ethynyl-2-oxetanone
f	4	—CH=CH₂	4-vinyl-2-oxetanone
g	4	—CH=CH—CH₃	4-propenyl-2-oxetanone

^{a} See Fig. 1 for numbering convention.

has never been isolated owing to its thermal lability [4], whilst its 4-isopropenyl isomer and 4-vinyl-2-oxetanone (f in Table 1) are both stable at room temperature. It is also evident that ring stability depends strongly on substitution in superacidic medium [5]: the protonated form of 2-oxetanone is stable up to 25°C whilst 4-methyl-2-oxetanone opens up (with C—alkyl cleavage) at −50°C; as for 3,3-dimethyl-2-oxetanone, no ring protonated species was detected even at temperatures as low as −80°C. Finally, new aspects of the reactivity of unsaturated β-lactones in transition-metal catalyzed reactions were reported by Noels et al. [6].

Our aim in this paper is to find an interpretation of the fact that conjugated substituents (e.g., e, f and g in Table 1) undergo ring opening with CO_2 release at a substantially faster rate than do compounds with saturated substituents at the same position.

$$\text{(structure)} \quad \rightarrow CO_2 + CH_2=CHR$$

To achieve this, a comparative ab initio study of seven 3- and 4-substituted 2-oxetanones (Table 1) was carried out at a uniform level of molecular orbital theory within a minimal STO-3G-basis set.

The paper is organized as follows: the general methodology used for MO-calculations is summarized; a detailed analysis of the electronic structure of the non-substituted 2-oxetanone ring and a comparison with other theoretical calculations and experiments (when available) is given; finally, the analysis of the electronic substitution effects, and their influence on the chemical reactivity of 4-substituted 2-oxetanones is investigated.

THEORETICAL METHODOLOGY

The equilibrium structural parameters of the molecules listed in Table 1 were determined by locating the minima of the potential energy surfaces

within the Born—Oppenheimer approximation. The number of degrees of freedom, $3n - 6$ (where n is the number of atoms) was too large for a complete geometric optimization. Hence, reasonable constraints to the geometric parameters were imposed for substituted derivatives by fixing C—H bond lengths to 1.09 Å.

Calculations were made at the Restricted Hartree—Fock' (RHF) level of the electronic theory. At such a level, one considers the independent motion of a single electron in the electrostatic field of fixed nuclei, and in the averaged Coulomb and exchange fields due to all other electrons. This level of the theory results in the traditional molecular orbital (MO) language. Within this level of the theory, calculations have been performed at the STO-3G degree of sophistication in the LCAO expansion of the molecular orbitals [7]. In such a calculation, molecular orbitals are expanded in the occupied atomic orbitals (AO's) of the isolated atoms, i.e., $1s$ for hydrogen, $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$ for carbon and oxygen. In the STO-3G scheme, each Slater-type orbital (STO) is furthermore expanded in linear combinations of three gaussians. This popularized basis set was introduced by Pople [7]. Its parameters (coefficients and exponents of the gaussian expansion) were carefully optimized to reproduce selected (molecular) properties such as molecular geometry. The advantages of this basis set are summarized in a review paper [8]. Moreover, for qualitative interpretations, minimal basis sets have the great advantage of relating molecular properties to simple atomic parameters, and allow for a conceptual approach common to both theoreticians and experimentalists.

All calculations have been made using the Gaussian series of programs [9]. All integrals $>10^{-6}$ a.u. have been explicitly taken into account and the convergence threshold on all elements of density matrices was found to be $<0.510^{-4}$.

ELECTRONIC STRUCTURE OF β-PROPIOLACTONE (2-OXETANONE)

Ab initio results for β-propiolactone and related four-membered rings using the $7s—3p$ minimal basis set of Clementi have already been published [10]. A recent parallel but independent work provides detailed RHF geometry optimization results on 2- and 3-oxetanones, using 4-21G basis sets [11, 12].

Results of our STO-3G complete geometry optimization on 2-oxetanone are given in Table 2, and are compared with 4-21G theoretical results [11], with electron diffraction [13] and microwave spectroscopic experiments [14].

An overall agreement is noticed. However, STO-3G results differentiate both C—O ring bonds ($C_2—O_1$ = 1.413 Å, $C_4—O_1$ = 1.453 Å) in a substantially less important way than do 4-21G calculations ($C_2—O_1$ = 1.400 Å, $C_4—O_1$ = 1.497 Å); experimental values are identical ($C_2—O_1$ = $C_4—O_1$ = 1.45 Å by electron diffraction and 1.42 Å by microwave spectroscopy).

TABLE 2

Bond lengths (Å) in the 2-oxetanone ring resulting from a geometry optimization with STO-3G, 4-21G and 6-21G basis sets and corresponding experimental results

Bond distance	Work STO-3G	4-21G[a]	6-21G[b]	Electron diffraction[c]	Microwave spectroscopy[d]
C_3-C_2	1.550	1.539	1.537	1.53	1.52
C_3-C_4	1.540	1.551	1.555	1.53	1.52
C_2-O_1	1.413	1.400	—[e]	1.45	1.43
C_4-O_1	1.453	1.497	1.489	1.45	1.43
C_2-O_5	1.202	1.184	1.184	1.19	1.169
C_3H_6/C_3H_7	1.086	1.078	1.080	(1.09)[f]	(1.09)[f]
C_4H_8/C_4H_9	1.093	1.074	1.073	(1.09)[f]	(1.09)[f]

[a]Ref. 11. [b]Ref. 12. [c]Ref. 13. [d]Ref. 14. [e]Not available from ref. 12. [f]Assumed.

TABLE 3

Total energies of β-propiolactone with respect to basis set used (data in atomic units)

Basis set	STO-3G	$7s, 3p$[a]	4-21G	6-21G
Total energy	−262.20896	−264.51430	−265.00117	−265.26427

[a]Non-optimized geometric structure.

For the completeness, Table 3 compares total energies resulting from the four ab initio calculations. The $7s, 3p$ minimal basis set results are obtained from a non-optimized geometrical structure. This reinforces a well-known point; namely that a well-balanced minimal basis set (such as STO-3G) is able to yield more reliable geometries than more extended but less carefully optimized sets.

Table 4 gives the orbital energies obtained by the STO-3G, $7s, 3p$ and 4-21G (when available) basis sets. As expected from the variation principle, a larger basis gives more negative orbital energies. The orbital energies can be related to non-relaxed ionization potentials by Koopmans' theorem. As already indicated, comparisons with refs. 11, 12 are difficult due to the lack of data. Data from refs. 11 and 12 seem also inconsistent in some respect. For example, ref. 11 mentions orbital ionization potentials No. 18 at 13.82 eV and No. 19 (HOMO) at 11.75 eV when obtained in the 4-21G basis set while ref. 12, reports 6-21G orbital energies No. 16 at −0.558 a.u. (15.17 eV), No. 17 at −0.507 a.u. (13.79 eV), No. 18 at −0.450 a.u. (12.24 eV) and No. 19 at −0.432 a.u. (11.75 eV). It is hardly conceivable that going from 4-21G to 6-21G results in a 1.58 eV shift for orbital No. 18 (13.82 → 12.24 eV). It is probable that in ref. 11 an a'' (π-like) orbital lying between two a' (σ-like) orbitals has been missed.

Our STO-3G orbital energies (Koopmans' ionization potentials) are in

TABLE 4

Orbital energies (in eV) of 2-oxetanone (Koopmans' ionization potentials)

Assignment (C_s symmetry assumed)	STO-3G	STO-3G[b]	$7s, 3p$	4-21G[c]	6-21G[d]
$1a'$	552.16		560.67		
$2a'$	551.89		560.65		
$3a'$	304.01		315.47		
$4a'$	302.28		312.16		
$5a'$	301.31		311.20		
$6a'$	37.64		41.21		
$7a'$	35.55		38.64		
$8a'$	27.02		30.70		
$9a'$	23.29		26.33		
$10a'$	18.70		$21.34(1a'')$		
$1a''$	17.82		$21.34(10a')$		
$11a'$	16.79		20.01		
$12a'$	15.99		19.11		
$2a''$	14.25		17.44		
$3a''$	13.32	13.26	16.96		
$13a'$	12.92	12.86	16.23		15.17
$14a'$	11.89	12.03	15.41		13.79
$4a''$	9.41	9.37	$13.33(15a')$	13.82[a]	12.24
$15a'$	9.14	9.18	$13.06(4a'')$	11.75	11.75

[a]See comment in the text; this data is probably erroneous and should correspond to the $14a'$ level. [b]From Table 1 of ref. 15, results using the experimental geometry. [c]From Table 3 of ref. 11. [d]From Table 3 of ref. 12.

complete agreement with other STO-3G results obtained with the experimental geometry of β-propiolactone and given in ref. 15. Furthermore, they correlate well with $7s, 3p$ results except for two inversions (10 a'/1 a'' and 4 a''/15 a').

This last inversion is worth discussion since it corresponds to different behaviors of the HOMO. The σ—π separation of orbitals is strictly appropriate for planar molecules only. In the case of β-propiolactone, there is, strictly speaking, no σ—π separation due to the four hydrogens lying out of the plane of the four-membered carbon ring. However, for the sake of simplicity in the following discussions, the symmetric expansions with respect to the four-membered planar ring are referred to as σ-orbitals, while antisymmetric expansions with respect to that plane are referred to as π-orbitals.

Figure 2 reproduces a part of the photoelectron spectrum of β-propiolactone obtained with the He I resonance line as excitation source [15]. Water H_2O, Xe and Ar transition lines are indicated in the figure. According to ref. 15, the lowest ionization energy band is assigned, by comparison of its vibrational structure with that of many esters and ketones, to ionization
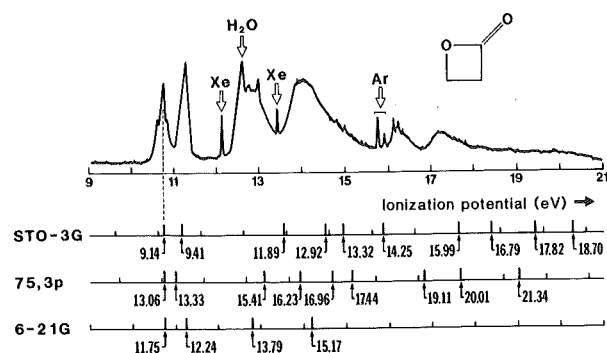
Fig. 2. UV photoelectron spectrum of β-propiolactone (adapted from ref. 15) and Koopmans' ionization potentials from STO-3G, 7s, sp and 6-21G calculation.

from an orbital having a lone-pair character. Table 5 shows the example of our computed HOMO ($15a'$). The second band refers to the ionization of endocyclic oxygen π-lone pairs ($4a''$). Third and fourth ionization bands refer to σ ($14a'$ and $13a'$ and π_{CO} -$3a''$) orbitals. Such an assignment is conformed by the LCAO expansion given in Table 5. In Fig. 2 we have also added our STO-3G one-electron eigenvalues, the previously published [10] 7s, 3p results and the available 6-21G orbital energies taken from ref. 12. Except for the shift due to basis set effects and to electron relaxation under ionization, our STO-3G and the 7s, 3p values are in fairly nice agreement with experiment.

Table 5 shows also that the first two LUMO's are of π*-(0.29 a.u./8.05 eV) and σ*-character (0.50 a.u./13.62 eV), respectively. This point is pertinent to the discussion in the next section.

ELECTRONIC STRUCTURE OF SOME 3- and 4-SUBSTITUTED-2-OXETANONES: A TENTATIVE EXPLANATION OF THEIR REACTIVITY

In order to identify some of the factors which influence the chemical reactivity of 2-oxetanones, static electronic indices for (a) 2-oxetanone, (b) 4-methyl-2-oxetanone, (c) 3-methyl-2-oxetanone, (d) 3,3-dimethyl-2-oxetanone, (e) 4-ethynyl-2-oxetanone, (f) 4-vinyl-2-oxetanone and (g) 4-propenyl-2-oxetanone are presented. (See also Table 1).

Optimized geometric results for the characteristic bonds of the 2-oxetanone ring present in the seven molecules listed above are given in Table 6, together with atomic populations and dipole moments.

A quick inspection of the content of this table demonstrates that the magnitudes of the properties are essentially independent of the type of substitution. Significant changes are found neither in the 2-oxetanone ring geometry (and thus on the stability and related properties such as bond strengths, force constants, etc.) nor in the total atomic charges. As is generally accepted, static indices are usually poor references from which to predict chemical reactivity.

TABLE 5

STO-3G one-electron energy eigenvalues, ϵ, and expansion coefficients of the higher occupied and lower unoccupied molecular orbitals of 2-oxetanone (UPS ionization potentials are given for comparison)

		Last occupied molecular orbitals					First unoccupied MO's	
ϵ(STO-3G) in a.u.		−0.4896	−0.4749	−0.4369	−0.3459	−0.3360	+0.2960	−0.5006
Koopmans' IP/EA in eV.		13.32	12.92	11.89	9.41	9.14	8.05	13.62
exp IP in eV (ref. 15).		14.02	←12.82→		11.30	10.78	—	—
C_2	1s		−0.019	−0.021		−0.008		−0.034
	2s		+0.121	+0.087		+0.020		+0.164
	$2p_x$		+0.163	+0.163		−0.097		+0.402
	$2p_y$	+0.503			−0.198		−0.826	
	$2p_z$		−0.331	+0.011		−0.129		+0.276
C_3	1s		+0.009	+0.021		−0.042		−0.048
	2s		−0.039	−0.093		+0.192		+0.256
	$2p_x$		−0.238	−0.392		+0.004		+0.436
	$2p_y$	−0.166			+0.067		−0.096	
	$2p_z$		+0.191	−0.018		+0.372		+0.113
C_4	1s		+0.027	−0.001		+0.06		−0.026
	2s		−0.141	+0.014		−0.031		+0.094
	$2p_x$		+0.319	+0.329		+0.026		+0.450
	$2p_y$	−0.182			−0.121		−0.006	
	$2p_z$		−0.264	+0.303		−0.026		+0.749
O_1	1s		−0.015	+0.059		−0.010		+0.097
	2s		+0.078	−0.309		+0.056		−0.588
	$2p_x$		−0.146	−0.218		+0.467		+0.211
	$2p_y$	+0.431			+0.769		+0.300	
	$2p_z$		+0.308	−0.484		+0.219		+0.533
O_5	1s		−0.044	−0.003				+0.006
	2s		+0.251	+0.026		+0.007		−0.038
	$2p_x$		−0.447	+0.239		+0.537		−0.203
	$2p_y$	+0.479			−0.532		+0.704	
	$2p_z$		+0.205	+0.263		+0.522		−0.097
H_6	1s	+0.143	−0.009	+0.128	−0.066	−0.097	−0.208	+0.097
H_7	1s	−0.143	−0.009	+0.128	+0.066	−0.097	+0.208	+0.097
H_8	1s	−0.143	+0.186	+0.050	−0.195	−0.001		−0.035
H_9	1s	+0.143	+0.186	+0.050	+0.195	−0.001		−0.035
Assignment		π_{CO}(a")	σ(a')	σ(a')	η_{O_1} (a')	η_{O_5} (a')	π*(a")	σ*(a')

In the recent years, mainly through the pioneering work by Fukui, the idea has emerged that preferred reaction paths could be explained on the basis of the nature and interactions of the Frontier Molecular Orbitals (FMO) of the involved molecules. Accordingly, Table 7 gives the energies and the main characteristics of the last two HOMO's and the first two LUMO's.

It is striking to note that the energy structure of the FMO's of the molecules studied divides into two distinct classes (A and B), as shown in Fig. 3. In both classes, the last two HOMO's lie in a narrow energy range (−0.32, −0.35 a.u.) while the first two LUMO's are non-degenerate in class A (+0.30, +0.50 a.u.) but are degenerate in class B (+0.30 a.u.).

It is furthermore interesting to note that all molecules of easy CO_2

TABLE 6

Bond lengths and electronic charges of the 2-oxetanone ring in some substituted 2-oxetanones (numbering of atoms same as in Fig. 1)
Dipole moments of some substituted 2-oxetanones

	2-Oxetanone	4-Methyl-2-oxetanone	3-Methyl-2-oxetanone	3,3-Dimethyl-2-oxetanone	4-Ethynyl-2-oxetanone	4-Vinyl-2-oxetanone	4-Propenyl-2-oxetanone
Bond length (Å)							
C_3C_2	1.550	1.549	1.551	1.552	1.550	1.550	1.549
C_3C_4	1.540	1.537	1.546	1.535	1.535	1.549	1.549
C_2O_1	1.413	1.409	1.414	1.417	1.414	1.420	1.410
C_4O_1	1.453	1.455	1.454	1.458	1.459	1.456	1.457
C_2O_5	1.202	1.203	1.203	1.202	1.201	1.203	1.203
Total electronic charges							
C_2	5.679	5.682	5.686	5.693	5.676	5.683	5.682
C_3	6.148	6.152	6.066	5.990	6.142	6.149	6.150
C_4	6.000	5.923	6.005	6.009	5.930	5.932	5.931
O_1	8.241	8.248	8.243	8.243	8.232	8.243	8.245
O_5	8.238	8.240	8.240	8.243	8.232	8.237	8.240
Dipole moment (debye)							
	2.96	3.08	3.05	3.10	2.84	3.04	3.31

release belong to class B while the others belong to class A. It is thus tempting to assume, for molecules in this class, a correlation between the orbitals of the propiolactone reagent and those of CO_2. An analysis of the LCAO expansion, Table 7, shows that, for all the lactones which do not release CO_2, the HOMO is of σ-character while in the three molecules which do release CO_2, the substituent induces an admixture of π-distribution into the HOMO (notice the zero $2p_y$ LCAO coefficients in the HOMO of class A and the non-zero coefficients in class B). A detailed analysis shows the same trends in the LUMO. Class A-LUMO's are only of π-character while class B-LUMO's exhibit mixed σ→π electron densities. To conform to the idea of a "preparation" of the MO's of the reactive lactones toward a carbon dioxide character, an STO-3G calculation on CO_2 (within its linear equilibrium geometry, $r_{C=O}$ = 1.16 Å) has been performed. It is found that the degenerate HOMO's are of π_g-character with an orbital energy of −0.393 a.u. while the LUMO's are also degenerate with π_u-character and have an orbital energy of +0.329 a.u. (c.f. +0.30 a.u. in reactive lactones). Figure 4 is a scheme of the HOMO structure of class A and class B lactones as well as one of the π_g-degenerate HOMO of CO_2. It is clear that in class B molecules there exists a π-moiety which has already the π_g-character parallel to a degeneracy of the two first LUMO's which correlates to π_u CO_2 LUMO's. In class A molecules, such a degeneracy of the LUMO's does not exist nor the above-mentioned moiety admixture. As can be observed from Fig. 4, the CO_2 release by class B lactones may be explained by the fact that in the reagent molecule, the orbital structure of CO_2 is "prepared" which appears to be a direct effect of the unsaturated substitution.

TABLE 7

Frontier orbital energies, ε, and corresponding LCAO expansion of the HOMO of 2-oxetanone and substituted-2-oxetanones

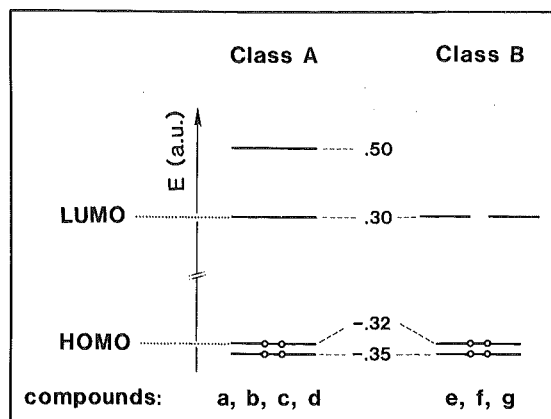|	2-Oxetanone	4-Methyl-2-oxetanone	3-Methyl-2-oxetanone	3,3-Dimethyl-2-oxetanone	4-Ethynyl-2-oxetanone	4-Vinyl-2-oxetanone	4-Propenyl-2-oxetanone
Frontier orbital energies (in a.u.)							
ε(HOMO)	−0.336	−0.332	−0.327	−0.320	−0.340	−0.329	−0.315
ε(HOMO−1)	−0.345	−0.340	−0.342	−0.341	−0.351	−0.337	−0.333
ε(LUMO)	+0.296	+0.299	+0.298	+0.301	+0.289	+0.294	+0.297
ε(LUMO+1)	+0.500	+0.496	+0.498	+0.500	+0.354	+0.297	+0.300
LCAO expansion in HOMO							
C_2							
$2s$							
$2p_x$	−0.09	−0.10	−0.10	−0.09	−0.08	−0.06	−0.06
$2p_y$							
$2p_z$	−0.13	−0.13	−0.15	−0.16	−0.13	−0.10	−0.17
C_3							
$2s$	+0.19	+0.18	+0.18	+0.15	+0.13	−0.14	+0.12
$2p_x$							
$2p_y$							
$2p_z$	+0.37	+0.38	+0.38	+0.39	+0.34	+0.24	+0.10
C_4							
$2s$							
$2p_x$							
$2p_y$					+0.08	+0.10	−0.06
$2p_z$							
O_1							
$2s$	+0.46	+0.46	+0.46	+0.45	+0.41	+0.27	+0.10
$2p_x$							
$2p_y$	+0.22	+0.21	+0.22	+0.22	+0.12	+0.22	+0.17
$2p_z$					+0.13	+0.05	−0.13
O_5							
$2s$	+0.57	+0.57	+0.51	+0.50	+0.50	+0.37	+0.20
$2p_x$							
$2p_y$	+0.52	+0.53	+0.51	+0.50	−0.07	−0.12	−0.09
$2p_z$					+0.50	+0.35	+0.20

Fig. 3. Distribution on the energy scale of the last two occupied and the first two unoccupied one-electron states. A comparison between class A (a, b, c, d) and class B (e, f, g) molecules.
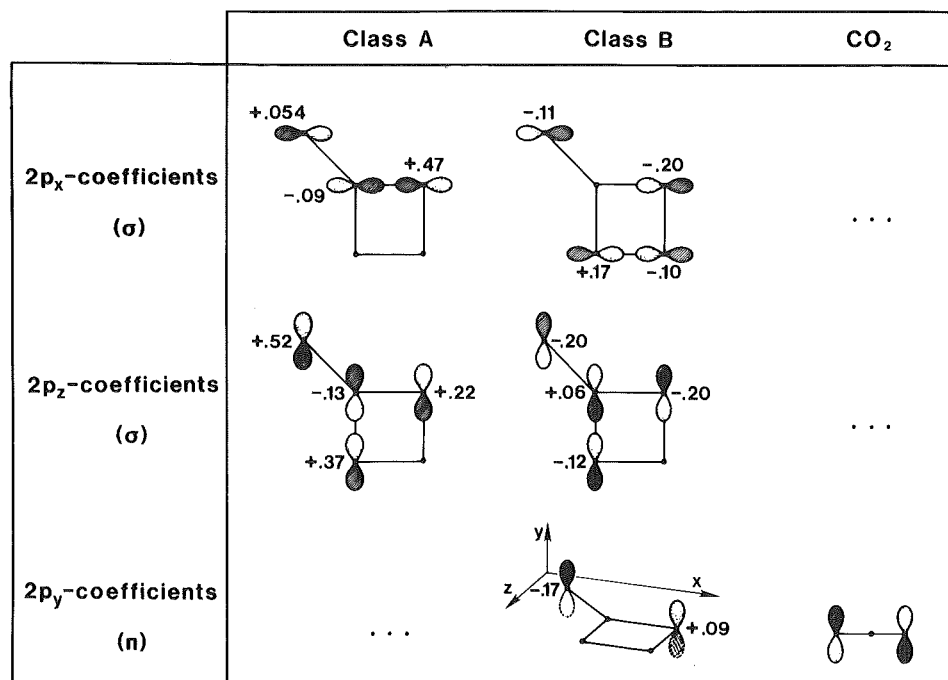

Fig. 4. Schematic structure of HOMO in class A molecules, class B molecules and CO_2.

CONCLUSIONS

In this work, using electronic structure calculations at the STO-3G level, and on the basis of the frontier orbital theory, we have been able to provide some insight as to the reaction trends observed in 2-oxetanone derivatives substituted with conjugated groups, as opposed to saturated ones. The main conclusion of this work is the observation of specific electron delocalization in conjugated derivatives, whose pattern directly correlates with that from products of the thermal decomposition. This is not found in the saturated derivatives.

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