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MOLECULAR ORBITAL CALCULATIONS OF EXCITED STATE CYCLOBUTANONE AND ITS PHOTOCARBENE

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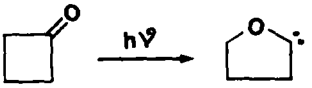
Abstract--Ab initio molecular orbital calculations at the MP2/6-31G*//6-31G* level are reported for cyclobutanone, acetone, and the isomeric oxacarbenes **2** and **3**; the first excited singlet states (S_1) of acetone and cyclobutanone have been calculated at the 6-31G* level using the UHF method. The cyclic oxacarbene **2**, lies 26 kcal/mol below the S_1 state of the isomeric cyclobutanone while the acyclic oxacarbene **3** is 2 kcal/mol above the S_1 state of acetone. Isodesmic reactions give the strain energies of cyclobutanone to be 24.9 kcal/mol in the ground state and 31.4 kcal/mol in the first excited singlet state.

INTRODUCTION

The Norrish type I process is a common primary photoreaction in cyclic ketones[1]. In cyclobutanones and other strained cyclic ketones, formation of an oxacarbene derived from ring expansion represents one of two competing processes (the other route being cycloelimination) and finds no counterpart in acyclic and unstrained cyclic ketones[2,3]. Furthermore, the two primary processes in cyclobutanone photochemistry are derived from the singlet state[4] whereas medium ring systems such as cyclohexanone undergo photochemical α-cleavage by way of the triplet state[5]. This unusual reaction in strained ketones has been rationalised in terms of orbital symmetry[6] and strain effects[6,3].



1 **2**

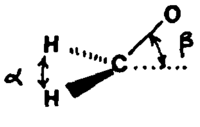
The orbital symmetry argument is based on the use of Salem correlation diagrams in which correlation between the singlet $n\rightarrow\pi^*$ state and a linear acyl diradical is proposed. This process, although symmetry allowed, is thermochemically untenable in unstrained cyclic ketones. By contrast, the strain associated with cyclobutanones and other constrained cyclic ketones such as certain bicyclo [2.2.1] heptanones permits such conversions on thermodynamic grounds. What is not clear is how a linear acyl alkyl diradical should lead to an oxacarbene. Quinkert[3] has used semiempirical perturbational methods to show that the 1, ω acyl alkyl diradical does not have to be invoked in this photochemical conversion and that the oxacarbene is directly derived from the singlet excited state of cyclobutanone. In order to gain a better understanding of this transformation and the nature of the cyclobutanone excited state and the oxacarbene we carried out ab initio molecular orbital calculations of these transients. Furthermore, we speculated that since carbonyl excited states involved non-planar geometries and that the deformation of the C-O bond from coplanarity may be a function of the X-CO-X angle then the X-O distance in excited cyclobutanone may be shorter than those in unstrained cycloalkanones and may facilitate bond formation between X and O. We have therefore carried out a similar study of acetone and the isomeric oxacarbene, CH_3OCCH_3.

RESULTS AND DISCUSSION

Standard ab initio molecular orbital calculations were performed using the MONSTERGAUSS[7] and GAUSSIAN-82[8] programs with the 3-21G basis set[9]. Single point calculations at the 6-31G* level[10] were carried out using optimized geometries derived from the 3-21G calculations. The ROHF method was used for the singlet state open shell calculations.

In order to establish whether the X-O distance is shortened in the singlet state upon contraction of the X-CO-X bond angle we performed calculations on the singlet state of formaldehyde at the 6-31G* level. The two angles α and β are defined as <H-C-H and the out-of-plane deformation angle of oxygen relative to the HCH plane. The S_1 optimized structure compares favourably with the experimental values[11]. These calculations at the 6-31G* level reproduce the experimental results more accurately than those reported by Kemper at the 4-31G/CI level[12].

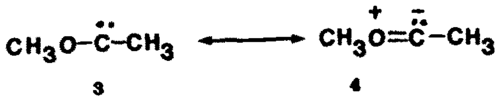
Table 1



α (exp)[11]	β (exp)[11]	O-H distance (exp)[11]
118.2 (118)	40.2 (33.1)	2.036Å (2.051)*
109.6	43.8	2.05Å
99.6	46.9	2.072Å
89.6	49.4	2.081Å

*calculated from exp. geometry in ref. 11

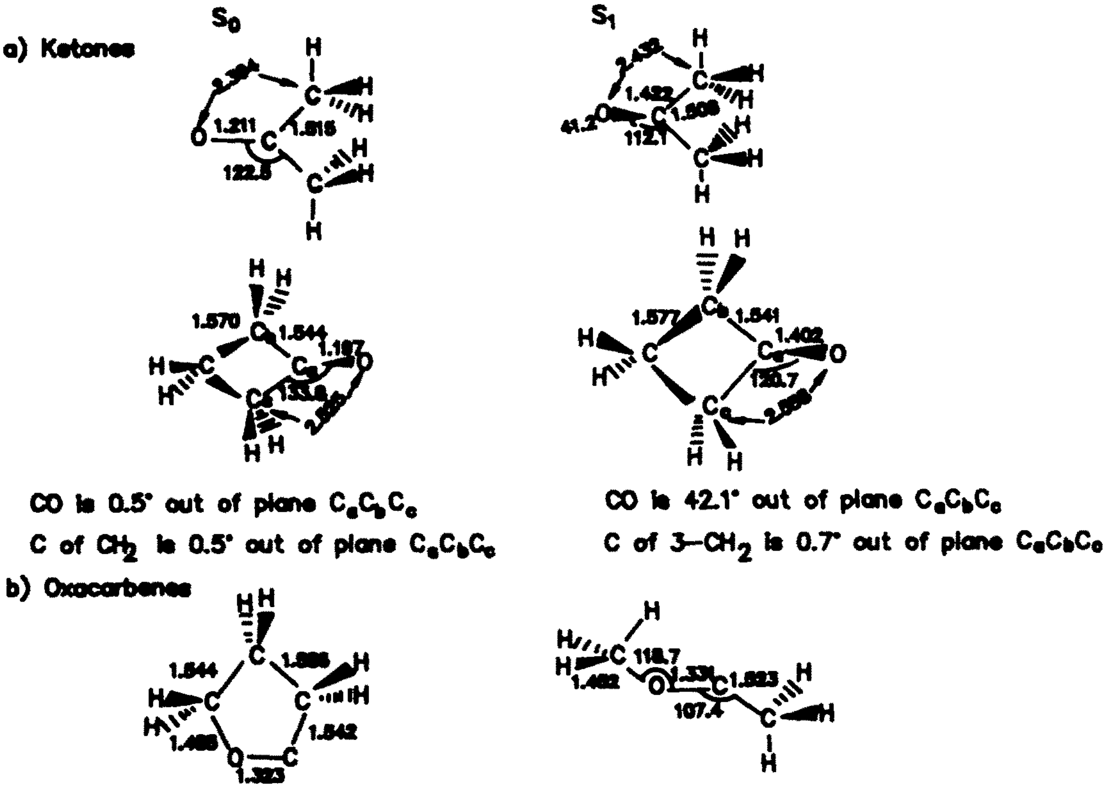
The angle α was then contracted and the remaining geometric parameters optimized. As expected, contraction of angle α increases the deformation angle β; however, at the same time the H-O distance increases with increasing non-planarity. This increase is principally due to the increase in the C-O bond length upon decreasing the angle α. It is interesting to note that the experimental H-O distance in singlet formaldehyde is longer (2.051Å vs 2.031Å) than that in the ground state in spite of deformation of the C-O bond from planarity in the excited state. This fact is in line with the increasing single bond character of the C=O function in the excited state. Subsequently we performed calculations on the ground and first excited singlet states of cyclobutanone (1) and acetone and on the oxacarbenes **2** and **3**. The excited molecules were examined at both their optimum structures and also at their ground state structures (the "Franck-Condon state).



$$\underset{\mathbf{3}}{CH_3O{-}\ddot{C}{-}CH_3} \longleftrightarrow \underset{\mathbf{4}}{CH_3\overset{+}{O}{=}\overset{-}{\ddot{C}}{-}CH_3}$$

The critical parameters from the structural optimisation are given in Figure 1. The calculated bond distances and angles for cyclobutanone compare favourably with experimental data[13]. The calculated geometry of ground state 1 shows a slight puckering with the C-3 methylene group 0.5° out of the plane defined by C_1-C_2-C_4.

FIGURE 1 Calculated Geometries of Ketones and Oxacarbenes



The potential surface for puckering of the cyclobutanone ring is very flat and the earliest microwave[14] and infrared[15] studies concluded that the ring is planar. Subsequent studies have shown the ring to be nonplanar but with a very low barrier to inversion 7.6±2 cm^{-1} [16,17], 5 cm^{-1} [18] and most recently 1.2±1.5 cm^{-1} [13]. By a combination of electron diffraction and spectroscopic data the potential minima were found to be a ring puckering angles of 10.4±2.7° [13]. This deformation is considerably larger than that given by the 3-21G basis set (0.5°), but the extremely flat surface makes exact location of the minima by molecular orbital theory very difficult.

On comparison of the excited state geometries of acetone and cyclobutanone it is interesting to note that the non-planarity of the C-O bond with the plane defined by the three bonded carbon atoms is comparable with that in excited formaldehyde. For both ketones the distance of the α-carbon from the carbonyl is slightly larger in the S_1 state than in the S_0 state (see Figure 1) and this increase is principally due to a substantial increase in the C-O bond length in the excited state which more than compensates for its deformation out of plane. There is no lengthening of the C_α-CO bond in either acetone or cyclobutanone singlet states and the speculation that the distance between the α carbon and the oxygen is shortened in the excited state of cyclobutanone, thereby facilitating oxacarbene formation, is not substantiated by these calculations.

Inspection of the structures calculated for oxacarbenes **2** and **3** clearly shows a shortened C-O bond length relative to normal C-O single bonds. This shortening is attributed to partial double bond character resulting from contribution of zwitterionic forms such as **4** in these species. The zwitterionic character of these oxacarbenes is substantiated by their chemical properties[19,20]. The ease of X-H insertion by oxacarbenes derived from cyclobutanones is directly related to the pKa of the X-H function[20].

Comparison of the energies of excited states of acetone, cyclobutanone and their corresponding oxacarbenes clearly indicate a thermodynamic effect for the difference

Table 2 - Relative Energies of Excited Species (kcal/mol)

Molecule	State	3-21G//3-21G	6-31G* (HF)	6-31G* (MP2)
H_2CO	S_0	0		
H_2CO	S_1	71.9 (4-31G)[a]		
H_2CO	S_1*[b](vertical trans.)	91.7 (4-31G)[a]		
HO-$\ddot{C}$H (trans)	S_0	52.5[a]		
$(CH_3)_2CO$	S_0	0	0	0
$(CH_3)_2CO$	S_1	50.4	62.8	
$(CH_3)_2CO$	S_1*[b](vertical trans.)	79.2		
CH_3-O-$\ddot{C}$-CH_3	S_0	59.4	65.1	73.8
1	S_0	0	0	0
1	S_1	56.8	66.7	
1	S_1*[b](vertical trans.)	82.9		
2	S_0	34.3	40.3	47.0
2	S_1	94.6		

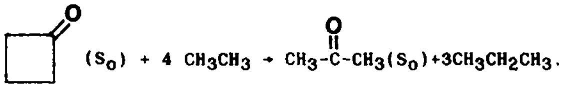
a. Values from ref. 23.

b. Singlet state with identical geometry to S_0.

* At ground state structure.

in photochemical behaviour. The oxacarbene **2** lies 22.5 kcal/mol below the optimized excited singlet state of cyclobutanone whereas **3** lies 9.0 kcal above the acetone singlet state at the 3-21G level (Table 2).

At the 6-31G* level the oxacarbene **2** lies 26.4 kcal/mol below cyclobutanone singlet state and **3** is only 2.3 kcal/mol higher than singlet acetone. Taking acetone as a model for non-strained cycloalkanones it would appear then that the absence of oxacarbene formation can be attributed to thermochemical factors and the strain associated with cyclobutanones. In order to calculate the strain energy of cyclobutanone the group separation reaction method[21] was used to obtain the ΔE for the hypothetical reaction in the equation:



$$(S_0) + 4\ CH_3CH_3 \rightarrow CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3(S_0) + 3CH_3CH_2CH_3.$$

The strain energy for ground state cyclobutanone is calculated to be 24.9 kcal/mol and compares favourably with the experimental value of 24.5 kcal/mol[22]. Applying this method to excited state cyclobutanone (replacing S_0 by S_1 for both acetone and cyclobutanone) a value of 31.4 kcal/mol is obtained for the strain energy of **1** in the excited singlet state. This is consistent with the observation that the electronic transition for cyclobutanone is similar to that of acyclic and unstrained cycloalkanones[4] i.e. the strain is not removed by electronic excitation. It is interesting to note that previously reported molecular orbital calculations of hydroxymethylene, the corresponding oxacarbene derived from formaldehyde, place it at 19.4 kcal/mol below excited singlet formaldehyde[23] and there is indirect evidence that a short-lived intermediate such as hydroxymethylene may be involved in the gas phase photolysis of formaldehyde[24].

These results suggest that strain effects play a primary role in the cycloalkanone-oxacarbene photo-ring expansion and that these arguments may be applicable to other strained bicycloalkanone-oxocarbne photoisomerizations[24]. Other factors such as the barrier to conversion would also have to be considered. However this is not easily done with the available methods for calculations at the level performed in this study.

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