

-0.130 au (-0.330 D) in the plane, together with a small component (0.031 D) perpendicular to the plane as expected for the model we used. The direction is as if the structure is $\text{CH}_3^+\text{C}_6\text{H}_5^-$, in agreement with the conclusion of earlier writers. The magnitude agrees with the experimental value of 0.36 D.^{4b} On the other hand, our *population analysis* makes the CH_3 group total population *negative* by 0.102e (see Figure 5), even though the π part is +0.018e (Figure 4). While it seems possible that this effect is an artifact of the imperfection of the population analysis procedure, an examination of Figure 5 indicates that it may not be inconsistent with the charge distribution in the molecule. It seems possible that the polarities in the charge distribution in the ring can account for the overall direction of the dipole moment in spite of a negative CH_3 group.

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A Theoretical Study Concerning Mechanisms of the Molecular Rearrangement of Carbonyl Compounds to Oxacarbenes in the Lowest Triplet State

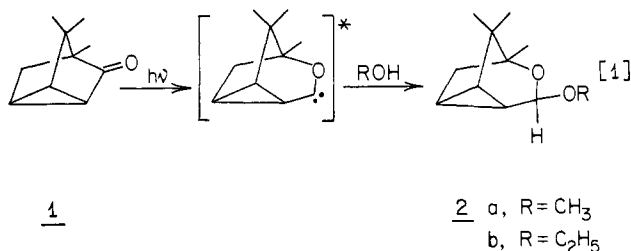
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Abstract: Nonempirical LCAO-SCF-MO calculations, applying a spin-restricted partitioned Hartree-Fock (PHF) method to open shells, have been carried out to investigate the effect of both basis set size and alkyl substitution on the mechanistic preference of the rearrangement of triplet carbonyl compounds to triplet oxacarbenes, as modeled by formaldehyde. Results suggest that the preference for the concerted pathway is independent of the size of the basis set. Substitution of an alkyl group for the migrating hydrogen changes the mechanistic preference from a concerted pathway to a diradical process. The relevance of these results to the rearrangement of cyclic ketones is discussed.

Introduction

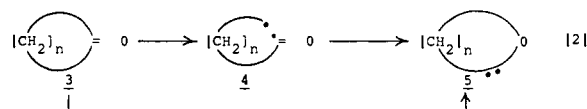
The name "oxacarbene" denotes a molecule that has an oxygen attached to a carbenic center. The formation of an oxacarbene as a reactive intermediate was first postulated by Yates and Kilmurry³ in connection with the photochemical conversion of cyclocamphanone (**1**) to ring-expanded acetals



2a and **2b**, respectively. Since this first report a considerable amount of research effort has been devoted to the study of this reaction. It was found that the formation of ring-expanded products is dependent on various structural features. There is a dichotomy⁴ in both the nature of the reactive excited states involved in this process and its mechanism.

Based on experimental evidence, it appears that some cyclic ketones react via their $n\pi^*$ singlet states,^{4,5} whereas others react via their $n\pi^*$ triplet states.⁶

Two mechanistic alternatives have been proposed to account for the photochemical transformation of cyclic ketones to oxacarbenes. One involves an α -cleavage of the carbonyl compound (**3**) to give a diradical species (**4**) which recombines at



oxygen to form the oxacarbene (**5**) (dissociation-recombination or diradical mechanism), and the other involves the formation of **4** directly from the excited ketone (concerted mechanism).

We have recently carried out a systematic ab initio study of the carbonyl-oxacarbene interconversion. In the first part of the study we investigated two distinct photochemical pathways (i.e., singlet and triplet) using formaldehyde as a model ketone. We reported⁷ that, according to our results, a concerted rearrangement in the triplet state is expected to be favored.

The present report is concerned with the investigation of the effect of both the size of the basis set and alkyl substitution on the mechanistic preference of the rearrangement:

Computational Details

All the computations were of the nonempirical LCAO-

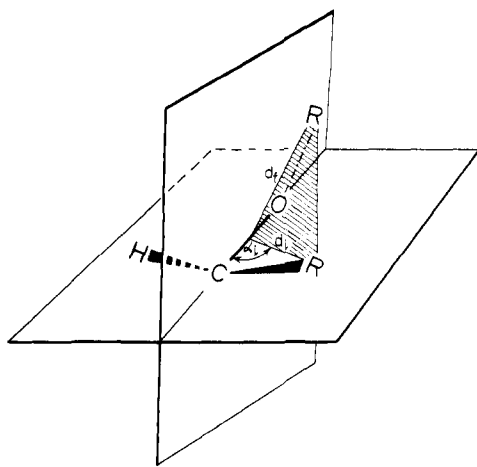


Figure 1. Unified internal coordinate system $\{d, \alpha\}$ used for the triplet carbonyl \rightarrow oxacarbene rearrangement. The shaded area corresponds to the migratory plane. (The initial values d_i and α_i as well as the final distance d_f are indicated on the figure. The regions investigated consist of reactant region $35^\circ \leq \alpha \leq 45^\circ$, central region $90^\circ \leq \alpha \leq 116^\circ$, and product region $135^\circ \leq \alpha \leq 145^\circ$.)

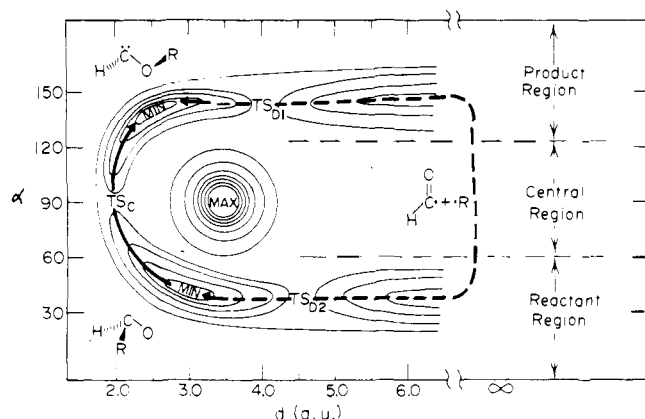


Figure 2. Topology of the photochemical rearrangement of triplet carbonyl compounds to triplet oxacarbenes.

SCF-MO type and were carried out on a CDC 7600 computer.

The triplet state energies were obtained by employing spin-restricted wave functions to open shells and by using a procedure in which the basis space is partitioned into orthogonal subspaces, and the energy is minimized by variation between these subspaces in successive steps. The mathematical basis for this particular method has been given by Dahl et al.⁸ and the corresponding program package was written by Robb.⁹

The basis set used was of uniform quality, optimized by Mezey,¹⁰ and consisted of five Gaussian *s* functions for hydrogen and a combination of (10s, 5p) Gaussian-type functions for carbon and oxygen. The contraction was carried out in such a fashion that the final set was of triple ζ quality with respect to the valence shell electrons and of double ζ quality with respect to the core electrons. The Gaussian exponents and the contraction coefficients are listed in Table I.

Results and Discussion

Description of Approach. The stereochemical approach taken for the present mechanistic study was designed to encompass both mechanistic alternatives (i.e., the diradical and concerted pathways). This was achieved by defining a migratory plane from three points: the spatial positions of the migrating atom (which may be part of a group) in both the

Table I. Uniform Quality Basis Set Exponents and Sester- (2.5) ζ Coefficients^b Used for the Mechanistic Study of the Carbonyl-Oxacarbene Rearrangement by the PHF Method

Atom	Gaussian function	Exponent	Contraction coefficient
Hydrogen	s_1	33.632 628	0.031 237 5
	s_2	5.078 436	0.209 427 1
	s_3	1.157 378 1	0.977 325 2
	s_4	0.325 758 53	1.0
	s_5	0.102 791 38	1.0
Carbon	s_1	8865.832 42	0.000 989 3
	s_2	1313.4599	0.007 782 1
	s_3	295.644 42	0.040 506 2
	s_4	82.818 509	0.159 134 1
	s_5	26.626 378	0.461 684
	s_6	9.341 051 1	0.871 678 7
	s_7	3.444 587 8	1.0
	s_8	1.007 362 2	1.0
	s_9	0.390 650 41	1.0
	s_{10}	0.133 640 98	1.0
	p_1	18.321 706	0.049 881 2
	p_2	4.050 723 7	0.290 015 2
	p_3	1.180 654 4	0.955 721 2
	p_4	0.377 675 58	1.0
	p_5	0.119 460 23	1.0
Oxygen	s_1	16 027.215	0.000 482 1
	s_2	2379.8774	0.003 788 9
	s_3	535.620 37	0.019 731 5
	s_4	150.376 33	0.077 493 7
	s_5	48.508 681	0.226 450 3
	s_6	17.101 827	0.429 984
	s_7	6.330 852 2	1.0
	s_8	1.835 862 5	1.0
	s_9	0.711 807 49	1.0
	s_{10}	0.243 350 62	1.0
	p_1	34.429 388	0.014 9135
	p_2	7.751 137 1	0.093 322 4
	p_3	2.280 312 3	0.286 325 6
	p_4	0.715 424 22	1.0
	p_5	0.213 830 67	1.0

^a Reference 10. ^b P. G. Mezey, private communication.

reactant and the product, and the center of mass of the reactant.¹¹ This is illustrated in Figure 1. The angle between the migratory plane and the horizontal plane was calculated to be 74.3° , and corresponds to the plane in which the concerted migration of a hydrogen was found (cf. previous report⁷) to take place with the lowest activation energy. The two mechanistic pathways could now be unified by envisaging a competition between the concerted migration and the dissociation-recombination taking place in the same plane. The motion of the migrating moiety in that plane may be characterized by two parameters, d and α , the distance between the migrating moiety and the center of mass and the in-plane displacement angle, respectively. This unified internal coordinate space spanned by d and α allows one to study the two possible mechanisms as two distinct paths on the energy surface

$$E = E(d, \alpha)$$

Based on this stereochemical approach, one can illustrate the topology of the expected triplet energy surface for the carbonyl-oxacarbene conversion as shown in Figure 2. The surface has three regions of minimum energy; two of these, associated with the reactant and the product, are relatively deep and close to each other. The third minimum, situated far away from the other two, is the highest and shallowest, and corresponds to the radical pair (or diradical) intermediate.

Table II. Variation of the Total Energy as a Function of Distance d^a and Angle α^a at Various Regions of the Migration Surface for the Formaldehyde Model System

Distance d , Bohr	Reactant region			Central region	Product region		
	$\alpha = 35^\circ$	$\alpha = 40^\circ$	$\alpha = 45^\circ$	$\alpha = 90^\circ$	$\alpha = 135^\circ$	$\alpha = 140^\circ$	$\alpha = 145^\circ$
1.5	-112.519 92	-112.901 18	-113.157 88	-113.629 40	-113.285 37	-113.036 65	-112.540 93
2.0	-113.421 55	-113.539 02	-113.617 56	-113.661 81	-113.672 09	-113.612 26	-113.513 35
2.5	-113.729 38	-113.752 73	-113.764 32	-113.652 22	-113.753 94	-113.755 24	-113.747 00
3.0	-113.772 86	-113.772 31	-113.766 53	-113.629 53	-113.718 14	-113.729 75	-113.677 02
3.5	-113.736 35	-113.731 21	-113.722 77	-113.624 13	-113.660 39	-113.669 75	-113.738 03
4.0	-113.682 82	-113.678 21	-113.671 19	-113.635 26	-113.649 83	-113.648 21	-113.646 09
4.5	-113.640 22	-113.638 29	-113.641 32	-113.641 44	-113.658 65	-113.657 70	-113.656 48
5.0	-113.648 43	-113.640 42	-113.652 55	-113.644 64	-113.663 50	-113.665 62	-113.662 45
5.5	-113.657 56	-113.658 58	-113.569 66	-113.646 18	-113.665 84	-113.663 02	-113.665 37
6.0	-113.662 45	-113.662 93	-113.663 45	-113.646 95	-113.666 96	-113.666 87	-113.666 76
28.0	-113.710 07 (bent)		-113.670 42 (linear)				

^a For the definition of distance d and displacement angle α , see Figure 1.

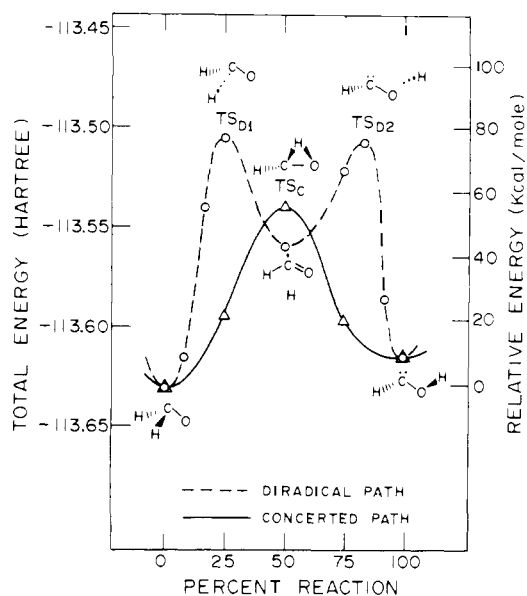
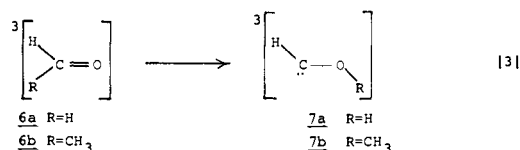


Figure 3. A comparison of the diradical and the concerted reaction energy profiles for the rearrangement of triplet formaldehyde to triplet hydroxycarbene. (Energy values were computed at the 4-31G level within the UHF formalism.⁷)

Each two of these regions are joined by a saddle point (TS) and each two of the saddle points are separated by a common maximum region. For a concerted rearrangement a direct route via TS_C is taken. In the case of the diradical mechanism, the reactant dissociates through TS_{D2} to the highest minimum, and then the recombination step takes place via TS_{D1} . The preferred mechanism, therefore, depends on the relative heights of these three saddle points. Based on the above, our study involved the examination of various reaction paths between all possible pairs of minima in order to locate the relevant saddle points. Comparison of the relative heights of these saddle points for rearrangements of the two different compounds (i.e., **6a** \rightarrow **7a**; **6b** \rightarrow **7b**) gives information about the



effect of alkyl substitution on the mechanistic preference. Further, comparison of the favored mechanistic pathway for the formaldehyde ($R = H$) with that from our previous work⁷

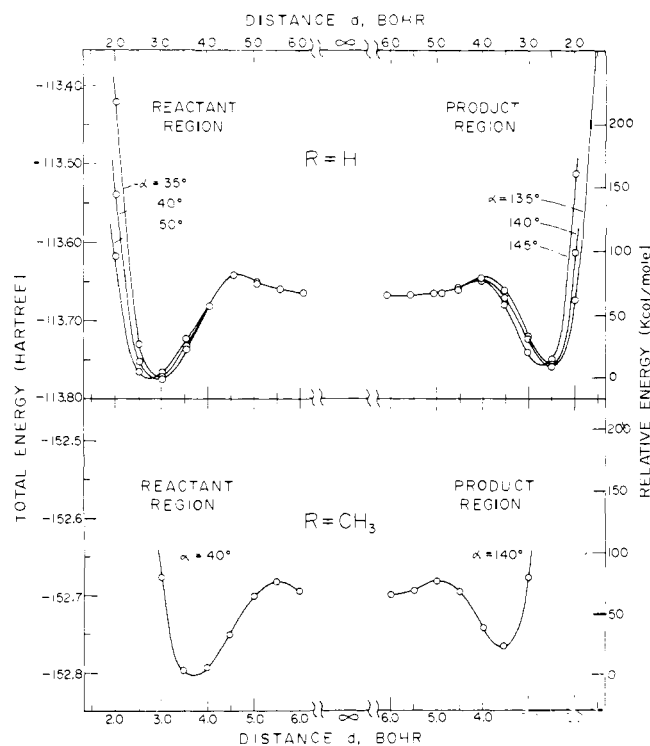


Figure 4. Cross sections at the reactant and product regions of the $E = E(d, \alpha)$ energy surface associated with the molecular rearrangements of triplet formaldehyde and triplet acetaldehyde to the corresponding triplet oxacarbenes.

permits the examination of the influence of the basis set size on the predicted mechanistic preference.

Investigation of Reaction Pathways. The two distinct pathways, corresponding to the concerted and the diradical mechanisms, are illustrated schematically in Figure 2 and shown explicitly for the case of the formaldehyde molecule⁷ in Figure 3. These energy profiles were computed from a sesqui- (1.5) ζ basis set within the unrestricted Hartree-Fock (UHF) formalism, using different coordinate systems for the investigation of the diradical pathway and the concerted route. In contrast, the present treatment involved the use of a sester- (2.5) ζ basis set in conjunction with a spin-restricted Hartree-Fock method to open shells. Furthermore, the use of a unified internal coordinate system (α and d) guarantees that the computed energy profiles are comparable in all aspects.

The actual study consisted of the investigation of the approach of the migrating moiety (R) from infinity toward the molecular fragment, restricting the approach to the migratory

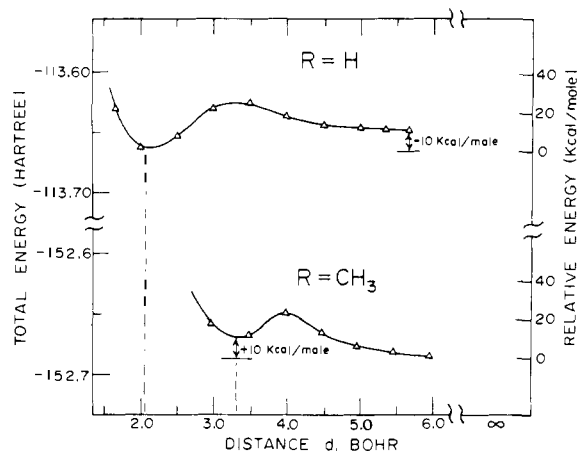


Figure 5. Central region cross sections ($\alpha = 90^\circ$) of the $E = E(d, \alpha)$ energy surface associated with the molecular rearrangements of triplet formaldehyde and triplet acetaldehyde to the corresponding triplet oxacarbenes.

plane (cf. shaded area in Figure 1), in three regions of the migration surface that are most probably involved in the rearrangement. These three regions are shown in Figure 2 and correspond to (1) the reactant region, (2) the product region, and (3) the central region. In the case of the formaldehyde molecule ($R = H$), three different pathways were examined in both the reactant and the product regions, corresponding to approaches from various directions (i.e., various values of α). In the central region only one path was considered, that which passes through the previously computed⁷ transition state (TS_c) for the concerted mechanism.

The results are summarized in Tables II and III and illustrated in Figures 4 and 5. From the upper part of Figure 4 it is apparent that in the neighborhood of the reactant and product conformations the direction of approach is relatively unimportant, since there is little change in the shape of the cross sections within a 10° variation of the in-plane displacement angle α . Consequently, for the case of acetaldehyde only one cross section was investigated for each region which was judiciously chosen from the above results. These are shown at the lower part of Figure 4.

Figure 5 shows the cross sections obtained for the approach of the migrating moiety toward the central region of the mo-

Table III. Variation of the Total Energy as a Function of the Distance d^a and Displacement Angle α^a at Various Regions of the Migration Surface Computed for the Acetaldehyde Model System

Distance d , Bohr	Total energy, hartrees		
	Reactant region $\alpha = 40^\circ$	Product region $\alpha = 140^\circ$	Central region $\alpha = 90^\circ$
2.5	-152.1460	-152.2059	
3.0	-152.6566	-152.6769	-152.6578
3.5	-152.7977	-152.7660	-152.6682
4.0	-152.7932	-152.7432	-152.6483
4.5	-152.7504	-152.6959	-152.6651
5.0	-152.7026	-152.6825	-152.6728
5.5	-152.6822	-152.6943	-152.6814
6.0	-142.6942	-152.7003	-152.6843
8.0	-152.7496 (bent)		

^a For the definition of the distance d and displacement angle α see Figure 1.

Table IV. Computed Barrier Heights in kcal/mol for HCHO and CH_3CHO Triplet Rearrangement Using Sesqui- (1.5) ζ and Sester- (2.5) ζ Basis Sets

Mechanism	Barrier ^a	HCHO		CH ₃ CHO
		E_a^b	E_a^c	E_a^c
Diradical	3 → 4	83.3	84.1	72.5
Diradical	4 → 3	41.6	45.0	42.3
Diradical	4 → 5	39.3	38.8	42.1
Diradical	5 → 4	67.0	67.2	52.4
Concerted	3 → 5	63.3	69.3	81.3
Concerted	5 → 3	49.3	53.5	61.4

^a Numbers shown correspond to the following type of species: 3, triplet aldehyde; 4 pseudodiradical; 5, oxacarbene (cf. eq 2 and Figure 7). ^b Barriers obtained using a 1.5 ζ basis set. ^c Barriers obtained using a 2.5 ζ basis set.

lecular fragment (i.e., $\alpha = 90^\circ$). As is apparent, the shapes of these curves, unlike those shown in Figure 4, differ substantially. The upper curve, associated with formaldehyde ($R = H$), indicates that the approach from infinity to the minimum (i.e., the transition state for the concerted path) is an exothermic process. This is to be contrasted with the curve ob-

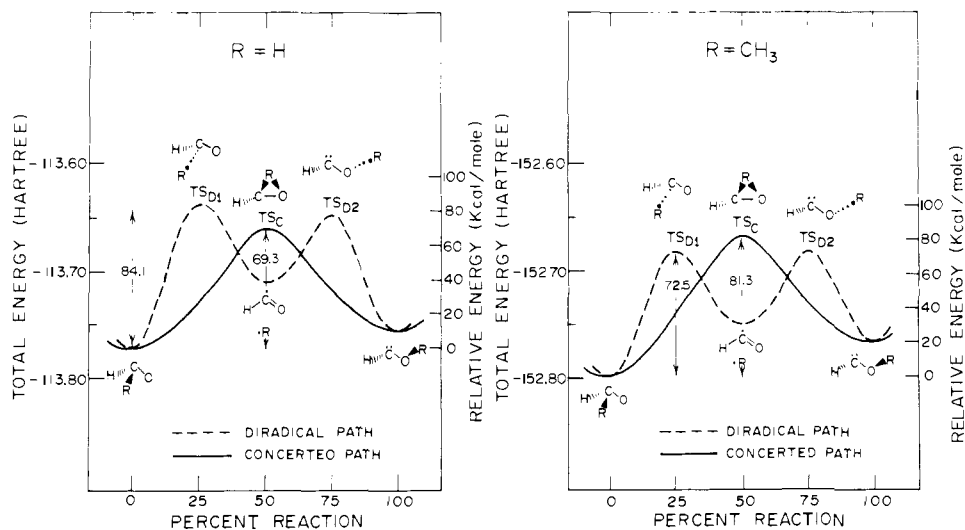


Figure 6. A comparison of the diradical and the concerted reaction energy profiles for the rearrangement of triplet formaldehyde ($R = H$) and triplet acetaldehyde ($R = CH_3$) to the corresponding triplet oxacarbenes. [Energy values (cf. Tables II and III) were computed at the sester- ζ (2.5 ζ) level within the PHF formalism.]

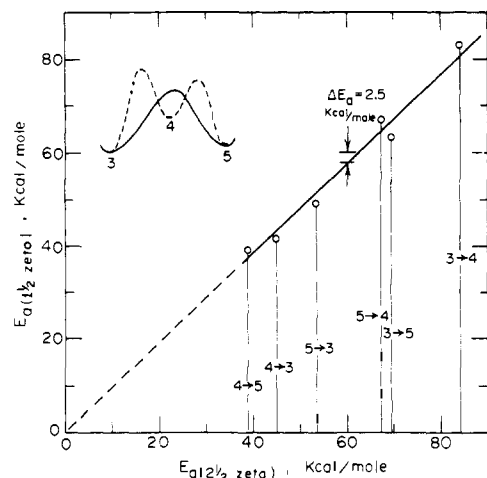


Figure 7. A graphical illustration of the basis set dependence of the computed barrier heights for the triplet formaldehyde \rightarrow hydroxycarbene rearrangement. The approximate discrepancy between the two basis sets for the average barrier height is shown to be 2.5 kcal/mol. [A schematic energy profile (cf. Figures 3 and 6) is shown at the upper left-hand corner including the structural labels 3, 4, and 5 defined in eq 2. The transitions $i \rightarrow j$ symbolize the barrier heights that interconnect the pairs of minimum i and j .]

tained for acetaldehyde ($R = \text{CH}_3$), in which the approach appears to be endothermic. Although the barriers associated with these curves are relatively low, their absolute energy value is much higher than those corresponding to the approach in either the reactant region or in the product region (cf. Figure 4). Therefore, the approach in this region is not expected to take place.

Combination of the results discussed above permitted the construction of reaction profiles for the two mechanistic alternatives, as shown in Figure 6. This figure reveals that for the formaldehyde molecule the barrier associated with the concerted pathway (TS_C) is significantly lower than the barriers corresponding to the dissociation-recombination mechanism, TS_{D1} and TS_{D2} , respectively. The situation is reversed, however, in the case of the acetaldehyde molecule. It is noteworthy that, despite this reversal, the barriers associated with the two mechanistic alternatives are very similar in magnitude to the corresponding values obtained for the formaldehyde model. The computed barriers clearly need not be the same¹² as the experimental activation energies estimated for cyclic ketones.

These results suggest that for alkyl migration the dissociation-recombination (or diradical) pathway is favored over the concerted migration. Thus substitution of a methyl group for the migrating hydrogen reverses the mechanistic preference.

In order to investigate the effect of the size of the basis set on the mechanistic preference, the results obtained previously⁷ have been reevaluated using the present method. Calculations have been carried out for all the critical points and selected intermediate points on the migration surface, using a basis set of 4-31G quality.⁷ The barriers to the various processes were

then recalculated and compared to those obtained using the large (2.5) ζ basis set. The results are summarized in Table IV and illustrated in Figure 7. According to the figure the points deviate very little from the "ideal" line with the slope of 1.0. In fact, the deviation ΔE_a , calculated for an average barrier of 60 kcal/mol, is only 2.5 kcal/mol. This suggests that the present results are essentially independent of the size of the basis set.¹³

Conclusions

The present work was concerned with the investigation of the mechanism of the rearrangement of triplet carbonyl compounds to oxacarbenes, as modeled by formaldehyde. In particular, the effect of both basis set size and alkyl substitution on the mechanistic preference has been examined.

It was found that the magnitudes of the computed barriers are virtually independent of the size of the basis set used. Consequently, the size of the basis set does not affect the preference for the concerted pathway reported earlier.⁷

However, substitution of a methyl group for the migrating hydrogen resulted in the reversal of the mechanistic preference. This could indicate that cyclic ketones will rearrange via the diradical mechanism. Nonetheless, there appears to be a very delicate balance between the relevant saddle points, which is influenced by structural factors.¹⁴ The validity of these predictions will be tested experimentally.

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- (11) It was found that the center of mass does not shift appreciably from reactant to product, and the position in the reactant was chosen arbitrarily.
- (12) This discrepancy is partly due to the fact that small cyclic ketones are significantly destabilized by ring strain.¹⁵ However, the most important factor influencing the height of the barriers in the present case is the computational method used. Since these barriers arise from avoided surface crossing,¹⁶ by virtue of mixing of the electronic states in the vicinity of the crossing point, the extent of mixing (i.e., the exact height of the barrier) can only be estimated with certainty by a multiconfigurational treatment. Single configurational methods (such as the one used for the present investigation) usually overestimate the barrier heights. Nevertheless, we believe that our *relative energetics* are meaningful and can be used to draw qualitative conclusions.
- (13) It should be mentioned, however, that the individual energy values, obtained from the computations involving the large basis set, decreased substantially (by ~ 90 kcal/mol).
- (14) Another explanation would be the following. The reversal of the mechanistic preference could indicate one of two possibilities: firstly, that cyclic ketones will rearrange via the diradical mechanism; and secondly, that the mechanism is influenced by structural factors. The former possibility implies that formaldehyde is not an ideal model for cyclic ketones, whereas the latter implies that no general mechanism can be predicted for the rearrangement. Although the first possibility appears to be more likely, further work, involving the study of the effect of additional alkyl substitution on the mechanism, is needed in order to make a definite prediction.
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