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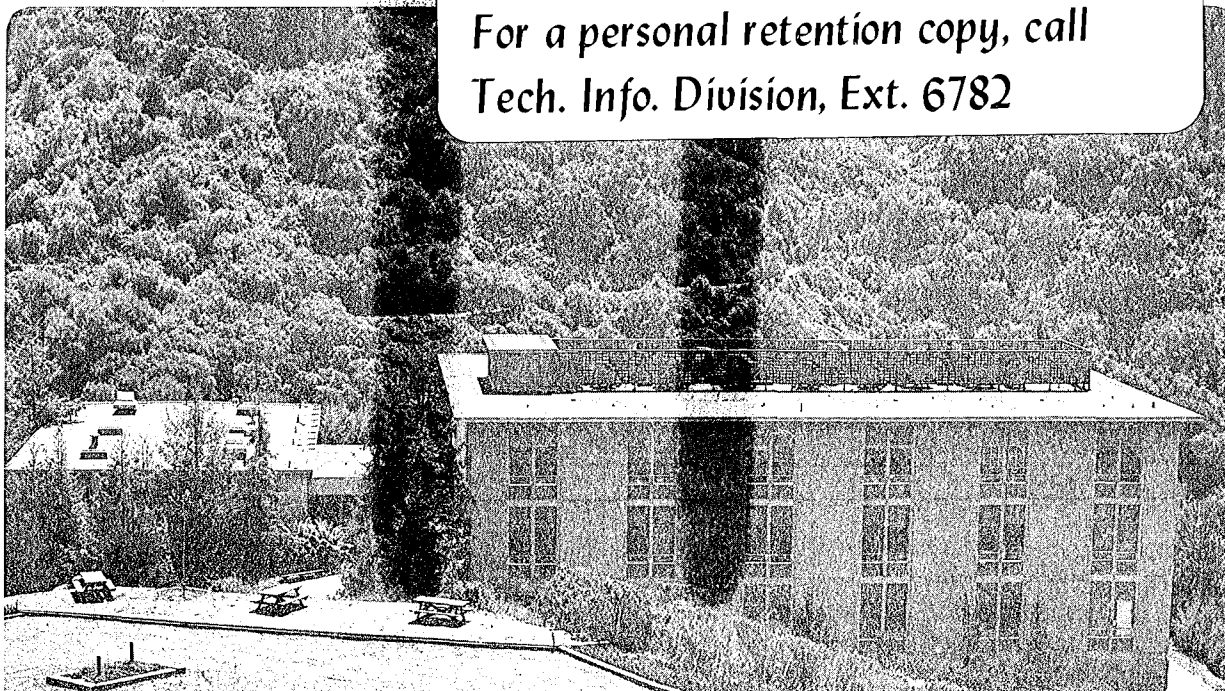
NEAR DEGENERATE REARRANGEMENT BETWEEN THE RADICAL
CATIONS OF FORMALDEHYDE AND HYDROXYMETHYLENE

Yoshihiro Osamura, John D. Goddard,
Henry F. Schaefer III, and Kwang S. Kim

June 1980

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Near Degenerate Rearrangement between the
Radical Cations of Formaldehyde and Hydroxymethylene

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Abstract

Motivated by the recent experiments of Berkowitz, a systematic theoretical study of the ion isomerization $\text{H}_2\text{CO}^+ \rightarrow \text{HCOH}^+$ has been carried out. Structures and vibrational frequencies for H_2CO^+ , the transition state, and the cis and trans isomers of HCOH^+ have been determined at the double zeta basis set self-consistent-field (SCF) level of theory. Equilibrium geometries were also predicted from SCF theory using a double zeta plus polarization (DZ + P) basis set. Final energetics were pinned down using DZ + P configuration interaction, involving a total of 16,290 configurations. The most reliable theoretical results suggest that trans HCOH^+ lies 5.5 kcal above H_2CO^+ . Zero-point vibrational energy corrections do not change this $\text{H}_2\text{CO}^+ - \text{HCOH}^+$ separation. Similarly cis HCOH^+ is predicted to lie 4.1 kcal above the trans isomer, and the barrier to rotation between the two HCOH^+ isomers is ~ 18 kcal. The barrier to $\text{H}_2\text{CO}^+ \rightarrow \text{HCOH}^+$ rearrangement is predicted to be 49.0 kcal, or 44.4 kcal after correction for zero-point vibrational energies is made. The relationship between this cationic 1,2 hydrogen shift and the corresponding neutral rearrangement is discussed in terms of qualitative molecular orbital theory.

Introduction

Recently Berkowitz has reported an interesting experimental study of the photoionization of CH_3OH , CD_3OH , and CH_3OD and used his data to discuss pertinent dissociative ionization mechanisms and ionic structures.¹ Probably the most intriguing result of Berkowitz's study is the conclusion that near threshold the process involving molecular hydrogen elimination leads to the structure HCOH^+ , rather than the anticipated formaldehyde radical cation H_2CO^+ . This experimental inference immediately raises the question, what is the energetic relationship between HCOH^+ and H_2CO^+ ? The corresponding neutral molecules have been the subject of state-of-the-art theoretical studies²⁻⁴ which suggest that HCOH lies ~52 kcal above H_2CO . Clearly, the experimental observations imply a much smaller energy separation between the positive ions of formaldehyde and hydroxycarbene. The purpose of the present research was to obtain definitive theoretical predictions for both the energy difference and the activation energy for the rearrangement



Several ab initio studies of HCOH^+ have been reported previously⁵⁻⁷ and these are summarized in Table I. The early work of Lathan et al.⁵ suggested that trans HCOH^+ lies 3-4 kcal below the cis isomer and ~12 kcal above H_2CO^+ . Using the Lathan equilibrium geometries, Dunning⁶ carried out double zeta plus

polarization (DZ + P) basis set self-consistent-field (SCF) calculations which reduced the $\text{H}_2\text{CO}^+ - \text{HCOH}^+$ separation to ~ 4 kcal. The only study to date of the transition state for (1) is that of Bouma, MacLeod, and Radom.⁷ They found an SCF barrier height of 82 kcal, which was reduced to 69 kcal when polarization functions were added to the basis set. The contribution of the present research is primarily the explicit consideration of electron correlation effects^{8,9} on these energy differences, and in addition the prediction of vibrational frequencies for the molecular species in question. Finally, it is hoped that the comparison of (1) with the analogous neutral isomerization



and the vinylidene rearrangement



will provide some helpful insights.

Theoretical Details

The theoretical approach adopted here was just that used in the work of Goddard and Schaefer³ on the corresponding neutral rearrangement (2). That is, geometrical structures were optimized using SCF (in this case open-shell¹⁰) gradient techniques and a double zeta (DZ) basis set,¹¹ designated C,0(9s5p/4s2p), H(4s/2s). Harmonic vibrational frequencies were subsequently

predicted at the same DZ SCF level of theory by diagonalizing the appropriate 12 x 12 matrices of (mass weighted) quadratic cartesian force constants.¹²

At the above determined and characterized stationary points, electron correlation was taken into account using the larger DZ + P basis set, which included sets of six d-like functions on C and O and a set of p functions (p_x , p_y , p_z) on H. With this DZ + P basis, configuration interaction (CI) including single and double excitations was carried out. The two lowest occupied SCF molecular orbitals were constrained to be "frozen" (i.e. doubly occupied) in all configurations and the two highest-lying virtual orbitals (core complements for a DZ + P basis) were deleted from the CI procedure. All remaining single and double excitations were included, yielding a total of 16,290 configurations in C_s symmetry (i.e. one plane only). As specified via the loop-driven graphical unitary group approach,^{13,14} this number of configurations refers to the Hartree-Fock interacting space only.¹⁵

The use of DZ stationary point geometries for single DZ + P CI calculations has recently been tested for the activation energies of (2) and



For these two reactions the structures of the reactants and transition states were explicitly optimized¹⁶ at the DZ + P CI level

using analytic CI gradient techniques.¹⁷ For (2) and (4) the activation energies thus predicted were 92.4 and 98.1 kcal, respectively. Earlier predictions based on the DZ geometries were 92.9 and 98.0 kcal. The errors resulting from DZ + P CI calculations at DZ SCF geometries are seen to be 0.5 and 0.1 kcal, in our opinion acceptably small. Therefore, one can be reasonably confident that the present predictions, based on a DZ + P CI/DZ SCF procedure, should be meaningful.

Results and Discussion

A. Stationary Point Geometries.

The DZ SCF geometries of H_2CO^+ , the transition state, trans HCOH^+ , and cis HCOH^+ are seen in Figure 1 and 2. Figure 1 shows that for all but the transition state, structures were determined at both the DZ and DZ + P SCF levels of theory. In general the agreement is reasonable between the two sets of predictions. For example, the addition of polarization functions to the basis uniformly decreases the C-O (by 0.030 Å, 0.019 Å, and 0.016 Å) and O-H (by 0.004 Å and 0.005 Å) distances and increases the C-H distances (by 0.005 Å in all three cases). The only serious disagreement between the DZ and DZ + P SCF results occurs for the C-O-H angles in trans and cis HCOH^+ . Specifically for the energetically lower trans isomer there is a difference

of $(127.2^\circ - 118.3^\circ) = 8.9^\circ$ in the two theoretical predictions. Fortunately, we know from analogous studies of H_2O ¹⁸ and other molecules¹⁹ that DZ-like basis sets can severely overestimate angles $\theta(AOB)$ about the oxygen atom. Therefore, we are confident that the DZ + P SCF values of $\theta(COH)$ are by far the more reliable for this particular geometrical parameter.

A comparison between the neutral and positive ion rearrangements is given in Figure 2. Perhaps the most obvious difference there occurs for the C-O bond distance in the trans isomers of HCOH (1.337 Å) and $HCOH^+$ (1.232 Å). The predicted neutral HCOH distance lies intermediate between typical C=O double bonds (e.g. H_2CO , $r = 1.21 \text{ \AA}$) and C-O single bonds (e.g. $H_3C-O-CH_3$, $r = 1.41 \text{ \AA}$).²⁰ That is to say, a conventional carbene valence structure of the type HC-OH underestimates the strength of the C-O bond. However, for the radical cation $HCOH^+$ it is apparent that the CO bond is much closer to being a true double bond. This suggests a qualitative valence structure of the type $\overset{\cdot}{H}C=O^+H$. Examination of the singly-occupied molecular orbital of trans $HCOH^+$ shows in fact that it is predominantly localized on the carbon atom.

Given the differences between the structures of H_2CO and H_2CO^+ and between HCOH and $HCOH^+$, the two transition states in Figure 2 are seen to be remarkably similar. For example, both involve roughly equilateral $\begin{matrix} & H & \\ & \diagdown & / \\ C & - & O \end{matrix}$ triangles. The CO distance for the neutral transition state is longer than for the ion

transition state, but this may be viewed as reflecting the analogous relationship between the two products HCOH and HCOH⁺. The only genuinely surprising prediction is the 137.1° HCO angle seen in Figure 2 for the H₂CO⁺ → HCOH⁺ transition state. A similar transition state angle (135.8°) was found by Bouma, MacLeod, and Radom. For the reactant H₂CO⁺ the analogous angle is 118.4° and for the product trans HCOH⁺ it is 127.1°. It is evident that no manner of least-motion mechanistic reasoning could predict such a transition state bond angle. This saddle point geometrical parameter actually moves well beyond its equilibrium product (or reactant) position as motion along the minimum energy path²¹ commences.

According to Hammond's postulate,²² one might expect the neutral transition state (neutral rearrangement is endothermic by ~52 kcal) to look more like the product HCOH than does the ionic transition state (ionic rearrangement is just a few kcal endothermic). However, except possibly for the HCO angles (discussed above) we find no evidence of this in Figure 2. Our only general conclusion about the relative shapes of these two transition states is that the ionic transition state structure is somewhat larger. That is, the distances between the migrating H atom and both the C and O atoms are longer at the ionic saddle point. Perhaps the simplest rationalization of this observation is that the CO distance is shorter for the ionic transition state and nature simply does not want these three atoms simultaneously close to each other. One's hope is that as more reliable data become

available for transition states, the sort of orderly understanding which characterizes structural chemistry will begin to emerge.

B. Energetics.

The present theoretical predictions for the relative energies of various H_2CO^+ species are summarized in the lower half of Table I. The DZ SCF predictions are rather close to the 4-31G results of Bouma, MacLeod, and Radom,⁷ as might be expected from the similarity of the two basis sets. The effect of polarization functions, as seen in the DZ + P SCF/DZ + P SCF results, is to lower the energies of HCOH^+ relative to H_2CO^+ . Specifically, the DZ + P SCF treatment predicts the trans isomer of HCOH^+ to lie only 5.7 kcal above H_2CO^+ . Correlation effects further reduce this separation, to 4.2 kcal using the DZ SCF equilibrium geometries or 3.8 kcal using the DZ + P SCF structures. The latter value is to be preferred, since the DZ SCF geometry predictions are flawed (as noted above) by their unrealistically large COH angles in trans and cis HCOH^+ . That is, the DZ SCF geometry predicted for H_2CO^+ is almost certainly significantly closer to its true equilibrium geometry than are the DZ SCF structures for the two HCOH^+ isomers. Finally, Table I shows that higher excitations (unlinked clusters)²³ increase $\Delta E(\text{H}_2\text{CO}^+ - \text{trans } \text{HCOH}^+)$ by 1.7 kcal to 5.5 kcal, our most reliable prediction. We suggest error limits of ± 3 kcal for this energy separation, and thus confirm Berkowitz's inference¹ that HCOH^+ is a very low-lying isomer of this positive ion.

At all levels of theory cis HCOH⁺ is predicted to lie slightly above the trans form. Furthermore this separation is consistently predicted to lie in the 3-4 kcal range. The smallest predicted separation (3.6 kcal) occurs at the DZ + P SCF/DZ SCF level, the largest (4.4 kcal) at the Davidson corrected DZ CI/DZ SCF level, and the most reliable (4.1 kcal) at the Davidson corrected DZ + P CI/DZ + P SCF level of theory. The barrier to rotational interconversion between the trans and cis isomers has also been examined. At the DZ + P SCF level this rotational barrier is ~ 18 kcal (starting from the trans side), which makes it nearly the same as the barrier to inversion about the oxygen center (i.e., making the COH angle 180°).

At the SCF level of theory, the classical barrier height is reduced by 16.8 kcal (from 83.2 to 66.4 kcal) when polarization functions are added to the basis set. CI including single and double excitations further reduces the barrier by 16.1 kcal, to 50.3 kcal. Use of Davidson's correction²³ yields our final prediction for the classical barrier height, 49.0 kcal. We suspect that a conservative estimate of the reliability of this barrier is ±5 kcal.

Comparison of the classical barrier heights for the H₂C=C:, H₂CO⁺, and H₂CO rearrangements (3), (1), and (2) is illustrative. The three predicted barrier heights are ~5,²⁴ ~50 (this work) and ~90³ kcal, respectively. Examination of the

molecular orbitals for the latter two transition states and for the triplet $\text{H}_2\text{C}=\dot{\text{C}}$ isomerization shows^{7,25} that changes in the $2b_2$ orbital of the reactants cause these high barriers. For the planar transition states this is the $7a'$ orbital. Bouma, MacLeod, and Radom⁷ specifically note that "the atomic orbital corresponding to the migrating hydrogen changes sign in the transition state, and indicates an avoided crossing of orbitals." Since this $2b_2$ or $7a'$ orbital is not occupied for the $14e^-$ system $\text{H}_2\text{C}=\text{C}$:, there is only a small barrier. For $\text{H}_2\text{C}=\text{O}$, however this orbital is doubly-occupied, yielding a very large barrier, ~ 90 kcal.³ For H_2CO^+ and triplet $\text{H}_2\text{C}=\dot{\text{C}}$ the $2b_2$ orbital is singly-occupied, and the resulting barriers are accordingly about halfway between 5 and 90 kcal.

C. Vibrational Frequencies

To allow direct comparison of the above energetic predictions with experimental observables (e.g. heats of formation, activation energies), it is in principal necessary to correct for the effects of zero point energy (ZPE). Furthermore, such corrections are not necessarily negligible. For example, for the neutral formaldehyde \rightarrow hydroxycarbene rearrangement (2), the transition state ZPE is 4.9 kcal less than for the reactant at the DZ SCF level of theory.

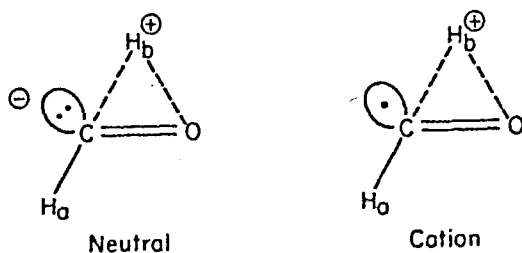
DZ SCF vibrational frequencies for H_2CO^+ , the transition state, trans HCOH^+ , and cis HCOH^+ are seen in Table II. From these one may predict ZPE's (in the harmonic approximation) of 17.46 kcal (H_2CO^+), 12.90 kcal (transition state), and 17.44 kcal (trans HCOH^+). Since the transition state ZPE is 4.56 kcal less than that of H_2CO^+ , this amount must

be subtracted from the classical barrier height (49.0 kcal) to yield the predicted activation energy of 44.4 kcal. Since the ZPE's of H_2CO^+ and trans HCOH^+ are essentially identical, the classical prediction of 5.5 kcal for this energy difference is unaffected.

D. Qualitative Considerations

The structural differences between the neutral molecule and the cationic species may be understood in terms of the shape of the active molecular orbital, which is also the HOMO for these systems. Figure 3 shows the qualitative change of the shape of the active MO during the rearrangements (1) and (2). This orbital is of course doubly occupied in the neutral and singly occupied in the cationic species. For the reactant H_2CO and H_2CO^+ moieties this $2b_2$ orbital is primarily 2p-like on the oxygen atom. Therefore removing one electron from this $2b_2$ orbital leads to an electron deficient character for the O atom and causes the smaller HCO angle in H_2CO^+ , owing to an attractive interaction between the CH bond and the nonbonding orbital on O.

Secondly we consider the large difference (19.8°) in transition state H_aCO angles between the neutral and cationic isomerizations. Analysis of the transition state wave functions suggest that the migrating hydrogen atom H_b has a considerable amount of protonic character. If the electronic structure at the transition state is naively considered as arising from the interaction between a proton and a formyl group, then the HCO fragment should be a formyl anion in the case of the neutral rearrangement transition state. Similarly the cationic species may be viewed as a formyl radical interacting with a proton



Furthermore the HCO angle of the formyl radical is known to be larger than that of the formyl anion. Hence this simple picture rationalizes the larger positive ion H_aCO angle (137.1° , see Figure 2) at the transition state.

Since the singly-occupied molecular orbital (SOMO) of both $HCOH^+$ and its transition state has the anti-phase combination on C and O atoms shown by Figure 3, the CO distances are shorter than in the neutral case. That is, the double occupation of this MO increases the anti-bonding character in the CO bond of the neutral. On the other hand, the π bond of HCOH has essentially the same character as that of $HCOH^+$. It is formed by the interaction between the empty $p\pi$ orbital on the C atom and the doubly occupied $p\pi$ orbital on the O atom. Therefore, it may be concluded that the difference in CO distances is based on the nature of the σ -type nonbonding orbital.

Concluding Remarks

The 1,2 hydrogen shift connecting the radical cations of formaldehyde and hydroxycarbene is very different from the corresponding neutral reaction. For the positive ion the HCOH^+ isomer is nearly degenerate (lying 5.5 kcal above) with the more conventional form H_2CO^+ . This result is entirely consistent with Berkowitz's recent experimental discovery that the photoionization of methanol leads to the HCOH^+ (rather than H_2CO^+) structure. Furthermore, the activation energy for the ion rearrangement (44.4 kcal) is much less than that for the neutral isomerization (88.9 kcal). Both barriers are "caused by" the $2b_2$ ($7a'$) molecular orbital of the reactants, and the double occupation of this orbital in the neutral rearrangement (as opposed to single occupation in the H_2CO^+) explains the difference in activation energies. As molecular ion spectroscopy continues to develop, it is hoped that the theoretical predictions made here will aid in the further experimental study of both H_2CO^+ and HCOH^+ .

Acknowledgements

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Table I. Relative energies in kcal/mole associated with the $\text{H}_2\text{CO}^+ \rightarrow \text{HCOH}^+$ isomerization. In describing the theoretical methods used, the designation

B/A is meant to imply that geometry optimization was carried out at level A, followed by single point calculations at the more complete level B.

Molecular Species	Absolute Energy (hartrees)	H_2CO^+	Transition State	$\frac{\text{trans}}{\text{HCOH}^+}$	$\frac{\text{cis}}{\text{HOCH}^+}$
Theoretical Method					
STO-3G/STO-3G ^a	-112.0958	0.0	----	22.2	25.8
4-31G/STO-3G ^a	-113.3411	0.0	----	11.5	15.3
DZ+P/STO-3G ^b	----	0.0	----	3.8	----
4-31G/4-31G ^c	-113.3421	0.0	81.8	9.1	----
6-31G*/4-31G ^c	-113.5140	0.0	69.1	9.7	----
This Research					
DZ/DZ	-113.4789	0.0	83.2	8.7	12.6
DZ+P/DZ	-113.5410	0.0	66.4	6.6	10.2
DZ CI/DZ	-113.6811	0.0	65.9	6.6	10.9
Davidson Corrected	----	0.0	64.8	8.4	12.8
DZ+P CI/DZ	-113.8077	0.0	50.3	4.2	8.4
Davidson Corrected	----	0.0	49.0	5.8	10.1
DZ+P/DZ+P	-113.5423	0.0	----	5.7	9.0
DZ+P CI/DZ+P	-113.8090	0.0	----	3.8	7.8
Davidson Corrected	----	0.0	----	5.5	9.6

^aReference 5.

^bReference 6.

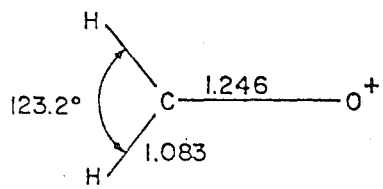
^cReference 7.

Table II. Predicted DZ SCF vibrational frequencies (cm^{-1}) for H_2CO^+ , HCOH^+ , and the transition state connecting them. The analogous neutral vibrational frequencies are given for comparison in parentheses.

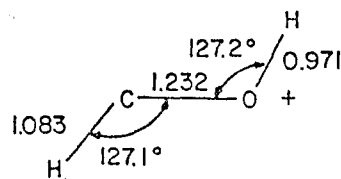
H_2CO^+	Transition State	<u>trans</u> HCOH^+	<u>cis</u> HCOH^+
$\nu_1(a_1)$ 3269 (3223)	$\nu_1(a')$ 3321 (3255)	$\nu_1(a')$ 3811 (4062)	$\nu_1(a')$ 3785 (3957)
$\nu_5(b_2)$ 3416 (3315)	$\nu_2(a')$ 2192 (2634)	$\nu_2(a')$ 3363 (3146)	$\nu_2(a')$ 3327 (2983)
$\nu_2(a_1)$ 1647 (1878)	$\nu_3(a')$ 1730 (1481)	$\nu_3(a')$ 1738 (1580)	$\nu_3(a')$ 1768 (1541)
$\nu_3(a_1)$ 1464 (1651)	$\nu_4(a')$ 1107 (1341)	$\nu_4(a')$ 1274 (1313)	$\nu_4(a')$ 1183 (1307)
$\nu_6(b_2)$ 1110 (1349)	$\nu_6(a'')$ 673 (621)	$\nu_5(a')$ 1017 (1265)	$\nu_5(a')$ 968 (1280)
$\nu_4(b_1)$ 1309 (1324)	$\nu_5(a')$ 3585i (2763i)	$\nu_6(a'')$ 997 (1087)	$\nu_6(a'')$ 969 (990)

Figure Captions

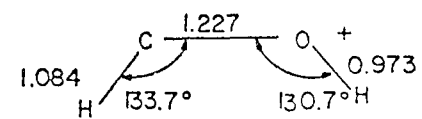
- Figure 1. Predicted equilibrium geometries of the formaldehyde radical cation and of the cis and trans isomers of hydroxycarbene radical cation. Bond distances are in Å.
- Figure 2. Comparison of reactant, transition state, and product geometries for the rearrangements $\text{H}_2\text{CO} \rightarrow \text{HCOH}$ (upper) and $\text{H}_2\text{CO}^+ \rightarrow \text{HCOH}^+$ (lower). Bond distances are in Å.
- Figure 3. Highest occupied molecular orbital (HOMO) for the formaldehyde \rightarrow hydroxycarbene isomerization.



DZ SCF

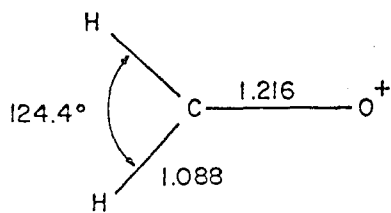


DZ SCF

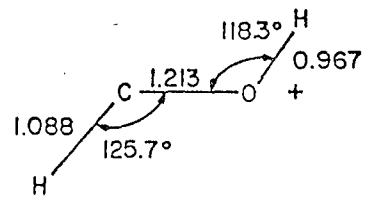


DZ SCF

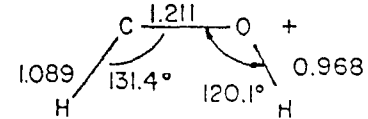
Figure 1



DZ + P SCF



DZ + P SCF



DZ + P SCF

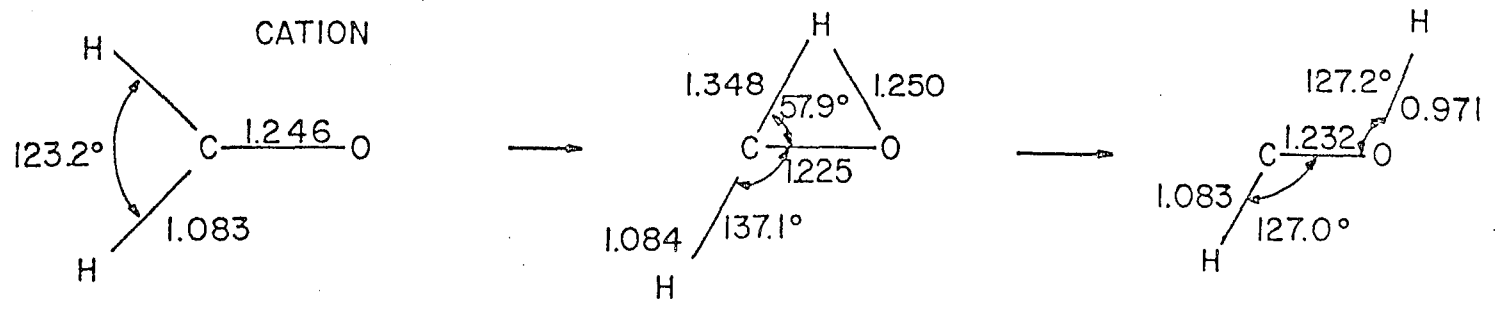
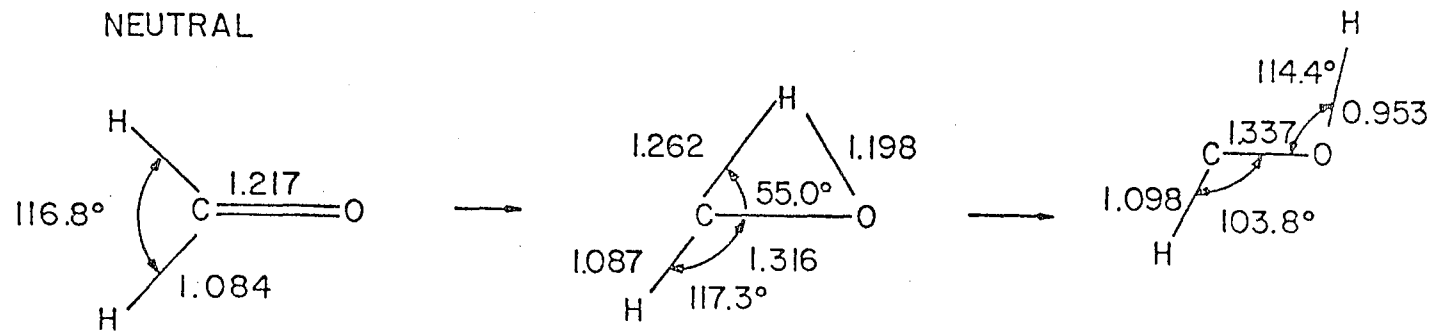
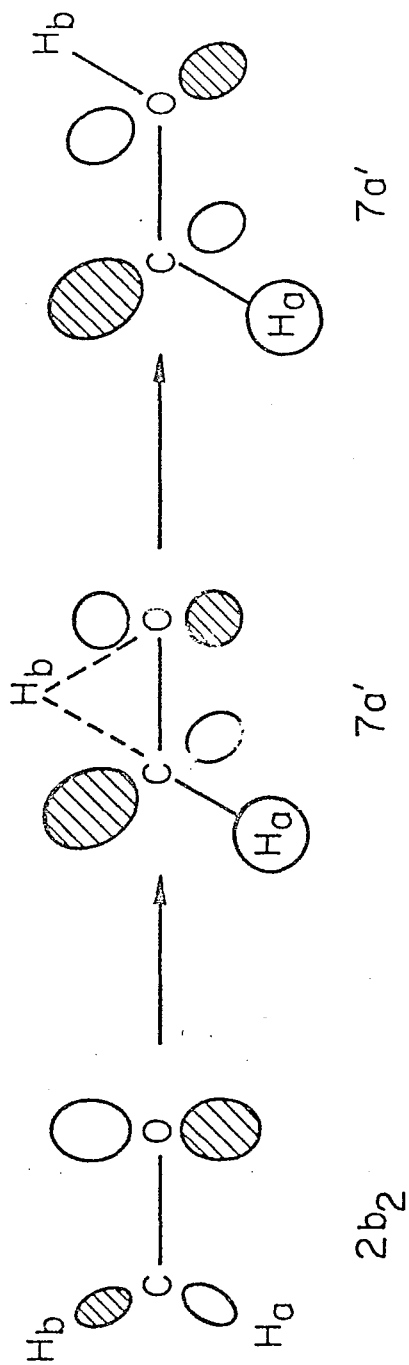


Figure 2



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Figure 3

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