

Table II. Energies (hartrees) of Different Isomers Related to HCON

state	isomer	-E
$^1A'$	HNCO <sup>a</sup>	167.7003
$^1A'$	HOCN <sup>a</sup>	167.6701
$^3A''$	HCON <sup>b</sup>	167.6338
$^1A'$	HONC <sup>a</sup>	167.5833
$^1A'$	HCNO <sup>a</sup>	167.5814
$^1A'$	HCNO <sup>b</sup>	167.4995

<sup>a</sup> Reference 17. <sup>b</sup> Present work.

agreement, we choose to make our comparison on the basis of the latter because our basis set and theirs are quite similar.

In order to better assess the quality of McLean's basis set as compared to ours, an SCF calculation was carried out on cyanic acid by using our DZ basis and the structural parameters given.<sup>18</sup> An energy value of -167.6698 hartrees was obtained as compared to -167.6702 hartrees of McLean et al., indicating that energy comparisons at that level can be made safely. In addition, the ground-state energy of the oxazirene molecule was calculated at a DZ-SCF level by using the partially optimized geometry of Rauk and Alewood.<sup>13</sup> Table II shows where formylnitrene, HCON, fits with respect to the rest of the isomers at a DZ-SCF level. Although all isomers, but HCON, are closed-shell singlets and going beyond the Hartree-Fock model would rather change the relative position of HCON in Table II, we believe that the latter corresponds to the lowest triplet state of all triplets which can be formed from the other isomers. This in turn suggests that by forming a triplet from one of the singlets of Table II, it would probably end on the triplet energy surface of HCON. Certainly, any dynamical effects are excluded from the above considerations.

## Conclusions

The principal conclusions of this study are as follows: (1) Both the formylnitrene and the formylphosphinidene are ground-state triplets. (2) Both molecules have two very closely spaced excited singlets. (3) The singlet-triplet splitting in the formylphosphinidene is smaller than in the formylnitrene. (4) The CN and CP bonds are oppositely polarized. (5) In the ground triplet and two low-lying singlet states the CN and CP linkages are essentially single bonds. (6) The carbonyl moiety remains essentially unaltered in going from HCON to HCOP.

Finally, we note that since the  $^3A''$  and  $^1A'$  states have been represented by single determinant SCF functions and the  $^1A'$  state by a pair of determinants, the possibility exists that the  $^1A'$  may be more correlated than the two SCF functions, resulting in an imbalance in the calculated separations. In this context it is worth repeating that for R-N or R-P molecules with cylindrically symmetric R groups this level of calculation would result in the  $^1A''$  and  $^1A'$  states being degenerate components of the  $^1\Delta$  state; i.e., they could be treated differently but equivalently. In the calculations we report the formyl group is essentially unconjugated with the N and P atoms, and consequently the  $\sigma$  and  $\pi$  orbitals (Figure 5) are essentially pure p orbitals on N and P. We expect therefore that any imbalance this treatment introduces would result in slight shifts (a few kilocalories) in the relative position of the reported levels. While this might alter the relative positions of the two singlets, perhaps even interchanging them, it would not change the above conclusions.

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## An ab Initio Study on Ketene, Hydroxyacetylene, Formylmethylene, Oxirene, and Their Rearrangement Paths

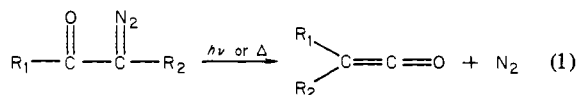
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**Abstract:** Ab initio quantum mechanical calculations on the singlet ground state of  $C_2H_2O$  have yielded geometries and rearrangement paths for ketene, hydroxyacetylene, formylmethylene, and oxirene. Geometries and rearrangement paths were determined by the single configuration self-consistent field method first by using the 4-31G basis set and then refined by using a double- $\zeta$  plus polarization basis set. Correlation energy corrections were calculated by using the configuration interaction method with a wave function which included all singly and doubly substituted configurations. The results show that hydroxyacetylene is 36 kcal/mol less stable than ketene, and there is a high barrier of 73 kcal/mol in the rearrangement path to ketene. Formylmethylene is unstable with respect to rearrangement to ketene, while oxirene is 82 kcal/mol above ketene with a small activation barrier of 2 kcal/mol for rearrangement to formylmethylene. These results together with preliminary results obtained for excited-state surfaces are used to elucidate the mechanism of the Wolff rearrangement. An analysis of the effects of polarization function and correlation energy on relative energy is also carried out to assess the accuracy of the results.

### I. Introduction

The mechanism of the Wolff rearrangement of diazoketones (eq 1)<sup>1,2</sup> has not been established unequivocally.<sup>3,5</sup> Wolff ori-



ginally proposed that the rearrangement should proceed via ke-

tocarbene intermediates.<sup>1</sup> In recent years, however, experiments using isotope-labeled diazoketones have indicated that oxirene may also participate as short-lived intermediates in photochemical<sup>5</sup> and thermal Wolff rearrangements.<sup>6</sup> The participation of oxirene

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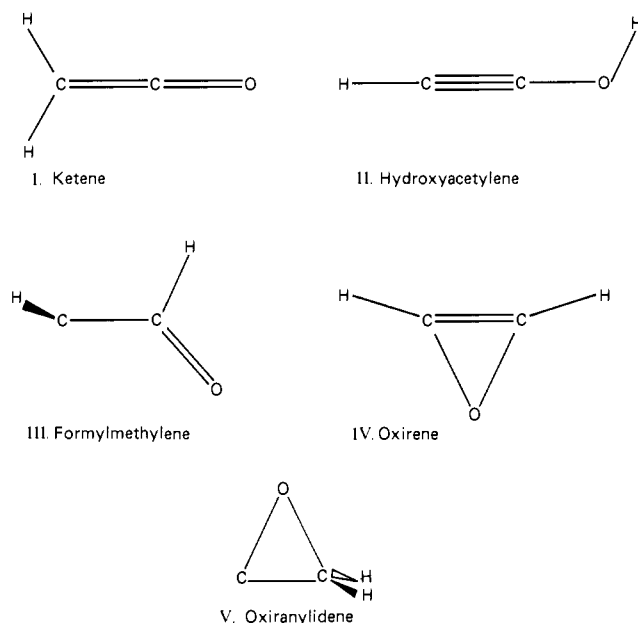


Figure 1. Structures of the  $C_2H_2O$  isomers.

in thermal Wolff rearrangement appears to be small but increases with increasing temperature.<sup>6</sup> Thus, with the assumption that ketocarbenes are primarily responsible for thermal Wolff rearrangements at low temperatures, it would follow that oxirene is higher in energy than its isomeric ketocarbenes. Also, Russell and Rowland<sup>7</sup> reported a yield of  $^{14}CO$  from the photolysis of  $^{14}CH_2CO$ , suggesting an oxirene intermediate in the photolysis of ketene.

However, no oxirenes have been isolated. Although ketocarbenes have been isolated in low-temperature matrices, these ketocarbenes have a triplet ground state.<sup>8</sup> Thus, there is no direct experimental evidence<sup>4,9</sup> for the role oxirene and ketocarbenes play in Wolff rearrangements which involve predominantly singlet intermediates.<sup>7,10</sup> Therefore, a theoretical calculation on the energies of the postulated intermediates and possible reaction can result in a significantly better understanding of the mechanism of the Wolff rearrangement.

There have been several ab initio SCF calculations on the ground state of  $C_2H_2O$ <sup>11-17</sup> and semiempirical calculations on  $C_2H_2O$  and related molecules.<sup>18,19</sup> For  $C_2H_2O$ , possible isomers are ketene (I), hydroxyacetylene (II), formylmethylene (III), oxirene (IV), and oxiranylidene (V); the structures of these isomers are sketched in Figure 1. Previous studies on the stabilities of

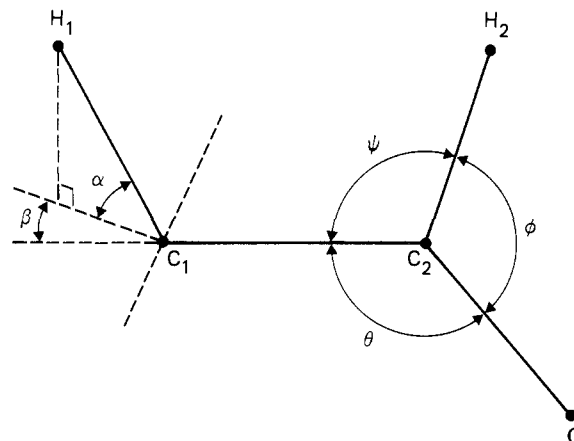


Figure 2. Definitions of geometrical parameters. All atoms except  $H_1$  are in plane.

these isomers and activation barriers for some of their rearrangement paths using the SCF method with double- $\zeta$  basis sets (SCF(DZ)) and semiempirical theory have been reviewed by Strausz et al.<sup>13</sup> The general conclusions appear to be that, at the SCF(DZ) level, oxirene is 86 kcal/mol less stable than ketene and formylmethylene is 15 kcal/mol more stable than oxirene. The activation barrier for the formylmethylene  $\rightarrow$  ketene interconversion is about 6 kcal/mol while that for the formylmethylene  $\rightarrow$  oxirene interconversion is about 19 kcal/mol. Oxiranylidene is as stable as formylmethylene, but there is a high barrier in the reaction paths going to formylmethylene and ketene.

Recently, Dykstra<sup>15</sup> reported a stability study of ketene, oxirene, and hydroxyacetylene by the SCF and SCEP methods. His results indicate that effects of polarization functions and electron correlation on isomer energies can be several kilocalories per mole and vary from isomer to isomer. Thus, it is necessary to take these effects into account for a reliable determination of the relative energies and activation barrier heights for the interconversions of these isomers.

The aim of the present study is to determine the energies of the  $C_2H_2O$  isomers so accurately that a definite understanding of the mechanism of the Wolff rearrangement and related processes may be obtained. For this purpose, we have investigated effects of polarization functions and correlation energy on the energies and rearrangement paths of the isomers: ketene, hydroxyacetylene, formylmethylene, and oxirene. Oxiranylidene was not studied because previous studies showed that it is not involved in these reactions due to a higher barrier for the rearrangement.

Another motivation for determination of the structure and energy of hydroxyacetylene is that this molecule, which has not been observed terrestrially, may exist in interstellar space. Molecular geometry predicted from ab initio calculation can be accurate enough to aid identification of this molecule in the interstellar medium, as were the cases for HNC and  $HCO^+$  (X-ogen).<sup>20</sup>

In this paper, we report the results of calculations on the singlet ground-state potential surface of the  $C_2H_2O$  system. Calculations on triplet and excited singlet surface are in progress, and only some of the preliminary results will be included here. The results for the structures and energies of the isomers of  $C_2H_2O$  together with a detailed analysis of effects of polarization and correlation are presented and discussed in section II. Rearrangement paths and activation barriers are presented together with preliminary results on excited states in section III. Finally, conclusions on the mechanism of the Wolff rearrangement and photolysis of ketene are presented.

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Table I. Basis Functions Included in DZ+P Calculations

atom	type	exponent	contractn coeff	
O	1s	10662.000 00	0.001 891	
	1s	1599.700 00	0.014 570	
	1s	364.730 00	0.074 020	
	1s	103.650 00	0.275 800	
	1s	33.906 00	0.719 550	
	1s	12.288 00	0.668 970	
	1s	4.756 80	0.367 310	
	1s	1.004 30	1.000 000	
	1s	0.300 69	1.000 000	
	2p	34.856 00	0.019 946	
	2p	7.843 10	0.125 170	
	2p	2.308 30	0.392 270	
	2p	0.723 16	0.627 730	
	2p	0.214 88	1.000 000	
	3d	0.850 00	1.000 000	
	C	1s	5240.600 00	0.002 050
		1s	782.200 00	0.015 830
		1s	178.350 00	0.079 820
		1s	50.816 00	0.288 040
		1s	16.824 00	0.703 070
1s		6.175 80	0.692 390	
1s		2.418 00	0.341 850	
1s		0.511 90	1.000 000	
1s		0.156 59	1.000 000	
2p		18.841 80	0.018 060	
2p		4.159 20	0.112 220	
2p		1.206 70	0.375 540	
2p		0.385 54	0.649 530	
2p		0.121 94	1.000 000	
3d		0.732 70	1.000 000	
H		1s	48.766 00	0.006 068
	1s	7.336 50	0.045 320	
	1s	1.668 70	0.202 850	
	1s	0.469 21	0.503 710	
	1s	0.147 95	1.000 000	
	2p	0.900 00	1.000 000	

## II. Structures and Energies of the Isomers

**A. Calculations.** Two sets of contracted Gaussian functions (CGF) were used in the present study. The first was the 4-31G basis of 31 CGF's used by Ditchfield et al.<sup>21</sup> The second was the double- $\zeta$  plus polarization (DZ+P) basis set of 58 CGF's used by McLean et al.<sup>22</sup> for calculations on the isoelectronic system HOCN. This set was constructed from atomic basis sets of van Duijneveldt,<sup>23</sup> C(9s5p), O(9s5p), and H(5s); the d functions had exponents of 0.7327 for carbon and 0.85 for oxygen; the p functions on H had an exponent of 0.9. The exponents and contraction coefficients for the DZ+P basis are listed in Table I.

Calculations were carried out by using both single configuration self-consistent field (SCF) and configuration interaction (CI) wave functions. The CI wave function included all singly and doubly excited configurations with respect to the closed-shell SCF configuration. The lowest three occupied orbitals, corresponding to carbon 1s and oxygen 1s orbitals, were kept doubly occupied and thus not correlated. Numbers of configurations for all isomers are listed in Table II.

Both SCF and CI wave functions were calculated by using the two basis sets described above. Thus, we employed four wave functions of different levels of approximation, designated as SCF(4-31G), SCF(DZ+P), SDCI(4-31G), and SDCI(DZ+P).

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Table II. Numbers of CSF's Used in the SDCI Calculations

isomer	sym	no. of CSF's	
		4-31G	DZ+P
ketene	C <sub>2v</sub>	3757	16 979
hydroxyacetylene	C <sub>s</sub>	7167	32 969
formylmethylene	C <sub>1</sub>	13041	62 481
oxirene	C <sub>2v</sub>	3621	16 583

This was done to investigate the effects of polarization functions and correlation energy corrections on the structure and stability of the isomers.

Geometrical parameters of each isomer were first determined by using the SCF(4-31G) wave function and then refined by using the SCF(DZ+P) wave function. For ketene, hydroxyacetylene and oxirene the geometry was further refined by using the SDCI(DZ+P) wave function. The SDCI(DZ+P) calculations on the formylmethylene  $\rightarrow$  ketene path yielded no potential barrier, and no further refinement of the formylmethylene geometry was performed.

Calculations were performed by using the GAUSSIAN 70 program system,<sup>24</sup> the direct CI program,<sup>25</sup> and the ALCHEMY program system.<sup>26</sup>

**B. Structures.** Geometrical parameters of the isomers of C<sub>2</sub>H<sub>2</sub>O obtained with various wave functions are given in Table III together with observed values<sup>27</sup> and results of previous calculations for comparison.

The SDCI(DZ+P) results for ketene are in excellent agreement with experimental results. The structures of hydroxyacetylene and oxirene are not known experimentally. The SDCI(DZ+P) results for these isomers are expected to be accurate to  $\pm 0.01$  Å for bond lengths and  $\pm 1^\circ$  for bond angles. There is no barrier in the SDCI rearrangement path from formylmethylene to ketene. Therefore, formylmethylene is unstable in spite of its apparent stability in the SCF approximation.

Except for oxirene, the effect of polarization functions on calculated bond lengths is small, shortening them by 0.01–0.02 Å. On the other hand, the effect of correlation energy is to increase calculated bond lengths by approximately the same amount. These results support the contention that SCF calculations with 4-31G or DZ basis sets yield reliable bond lengths for small organic molecules.<sup>28</sup> The effect of polarization functions on bond angles is as much as 7°. But the effect of correlation is small enough that the SCF(DZ+P) wave functions give reliable bond angles.

For oxirene, the effect of polarization functions is quite large, particularly for the C–O bond which is shortened by 0.08 Å. Dykstra has reported a similar shortening of the C–O bond, 1.548 and 1.467 Å in SCF(DZ) and (DZ+P) approximations, respectively.<sup>15</sup>

We note that our optimized structure of hydroxyacetylene is slightly nonlinear in the CCO atomic conformation and that the CH bond is trans to the OH bond in a planar molecule. The SDCI(DZ+P) results for the CCO angles is 177.8°, which is almost identical with the NCO angle of 177.7° obtained for the isoelectronic HOCN molecule.<sup>22</sup>

**C. Rotational Constants.** Table IV gives rotational constants calculated with the SDCI(DZ+P) wave functions for ketene, hydroxyacetylene, and oxirene and observed values for ketene.<sup>29</sup> The ketene results are in excellent agreement with observed values,

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Table III. Optimized Structures and Total Energies of the Lowest Singlet State of the C<sub>2</sub>H<sub>2</sub>O Isomers Calculated in Various Levels of Approximation

Approximations	Ketene						total energy		
	dist, <sup>a</sup> Å			angles, <sup>a</sup> deg					
	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -O	C <sub>1</sub> -H <sub>1</sub>	<H <sub>1</sub> C <sub>1</sub> H <sub>2</sub>					
SCF(4-31G)	1.297	1.164	1.070	120.0		-151.49493			
SCF(DZ) <sup>b</sup>	1.311	1.171	1.070	120.1		-151.67244			
SCF(DZ+P)	1.309	1.147	1.073	122.0		-151.76225			
SDCI(DZ+P)	1.319	1.167	1.077	122.2		-152.16008			
Exptl.	1.314	1.161	1.079	122.3					
	(±0.01)	(±0.01)	(±0.002)	(±0.2)					
	Hydroxyacetylene								
	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -O	C <sub>1</sub> -H <sub>1</sub>	O-H <sub>2</sub>	<C <sub>1</sub> C <sub>2</sub> O	<C <sub>2</sub> OH <sub>2</sub>			
	SCF(4-31G)	1.185	1.317	1.049	0.954	178.3	115.3	-151.44420	
SCF(DZ) <sup>b</sup>	1.193	1.322	1.051	0.953	180.0	115.6	-151.62738		
SCF(DZ+P)	1.186	1.302	1.059	0.948	178.4	110.3	-151.70628		
SDCI(DZ+P)	1.204	1.318	1.064	0.960	177.8	108.7	-152.10242		
	Formylmethylene								
	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -O	C <sub>2</sub> -H <sub>2</sub>	C <sub>1</sub> -H <sub>1</sub>	<C <sub>1</sub> C <sub>2</sub> O	Ψ	β	α	
	SCF(4-31G)	1.420	1.220	1.098	1.085	129.8	108.6	3.7	61.5
SCF(DZ) <sup>c</sup>	1.400	1.260	1.100	1.050	130.0	110.0	0.0	60.0	-151.55386
SCF(DZ+P)	1.429	1.193	1.111	1.089	129.6	107.7	10.2	69.0	-151.64910
	Oxirene								
	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -O	C <sub>1</sub> -H <sub>1</sub>	<C <sub>1</sub> C <sub>1</sub> O	<C <sub>1</sub> C <sub>2</sub> H <sub>2</sub>				
	SCF(4-31G)	1.248	1.552	1.054	66.3	162.3	-151.35397		
SCF(DZ) <sup>b</sup>	1.261	1.548	1.057	66.1	162.5	-151.53543			
SCF(DZ+P)	1.250	1.465	1.065	64.7	162.6	-151.62339			
SDCI(DZ+P)	1.270	1.491	1.071	64.8	162.1	-152.02890			

<sup>a</sup> See Figure 2 for definition of geometrical parameters. <sup>b</sup> Reference 15. <sup>c</sup> Reference 12.

Table IV. Rotational Constants (MHz) Calculated with our SDCI(DZ+P) Wave Functions

isomers	A	B	C
ketene	28 2040 (28 2081) <sup>a</sup>	10 218 (10 294) <sup>a</sup>	9860 (9915) <sup>a</sup>
hydroxyacetylene	66 4690	9 674	9535
oxirene	3 3265	26 719	14817

<sup>a</sup> J. W. C. Johns and J. M. R. Stone, ref 29. The observed values are given only to MHz here, although ref 29 gives more figures. Numbers in parentheses are observed values.

Table V. Total Energies (au) of the Isomers Calculated at the Geometries Optimized with SCF(4-31G), SCF(DZ+P), and SDCI(DZ+P) Wave Functions

geometry and basis set	SCF(4-31G)	SCF(DZ+P)	SDCI(DZ+P)
Ketene			
SCF	-151.49493	-151.76225	-151.76121
SDCI	-151.77929	-152.16007	-152.16104
SDQCI <sup>a</sup>	-151.80768	-152.20439	-152.20621
Hydroxyacetylene			
SCF	-151.44420	-151.70628	-151.70514
SDCI	-151.72651	-152.10242	-152.10359
SDQCI <sup>a</sup>	-151.75443	-152.14605	-152.14820
Oxirene			
SCF	-151.35397	-151.62339	-151.62207
SDCI	-151.64883	-152.02890	-152.03016
SDQCI <sup>a</sup>	-151.68131	-152.07593	-152.07839
Formylmethylene			
SCF	-151.37225	-151.64910	
SDCI	-151.64272	-152.03387	
SDQCI <sup>a</sup>	-151.67004	-152.07733	

<sup>a</sup> SCQCI results are obtained by adding the estimated correlation correction to the SDCI results.

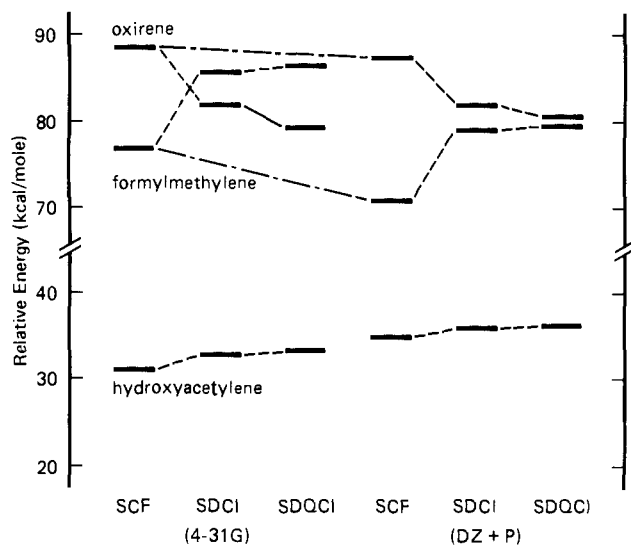
the errors being less than 0.1 GHz. We expect that our rotational constants for the other isomers are also accurate to within 0.1 GHz.

Table VI. Relative Energies (kcal/mol) of the Isomers with Respect to Ketene Calculated at the Geometries Optimized with SCF(4-31G), SCF(DZ+P), and SDCI(DZ+P) Wave Functions Together with Polarization Function and Correlation Energy Effects

geometry and basis set	SCF(4-31G)	SCF(DZ+P)	SDCI(DZ+P)
Hydroxyacetylene			
SCF	31.8	35.1	35.2
ΔE(SD)	1.3	1.1	0.9
SDCI	33.1	36.2	36.1
ΔE(Q)	0.3	0.4	0.3
SDQCI	33.4	36.6	36.4
Formylmethylene			
SCF	77.0	71.0	
ΔE(SD)	8.7	8.2	
SDCI	85.7	79.2	
ΔE(Q)	0.7	0.5	
SDQCI	86.4	79.7	
Oxirene			
SCF	88.5	87.2	87.3
ΔE(SD)	-6.6	-4.8	-5.2
SDCI	81.9	82.3	82.1
ΔE(Q)	-2.6	-1.7	-1.9
SDQCI	79.3	80.6	80.2

Hydroxyacetylene appears to be quite stable, due to a high barrier of 73 kcal/mol in the rearrangement path to ketene and a stability of 110 kcal/mol against dissociation to C<sub>2</sub>H(<sup>2</sup>Σ<sup>+</sup>) + OH(<sup>2</sup>Π). Although this isomer has not been observed terrestrially, it is likely to exist in dense interstellar clouds where C<sub>2</sub>H and OH molecules are known to be abundant. The rotational constants reported here should be useful in a search for hydroxyacetylene in interstellar space.

**D. Relative Energies.** Calculated total energies of the isomers of C<sub>2</sub>H<sub>2</sub>O are given in Table V, and relative energies with respect to ketene are given in Table VI together with effects of polarization functions and correlation energy, which are also depicted in Figure



**Figure 3.** Effects of polarization functions and correlation energy on the relative energies of the isomers. Dashed lines indicate the effect of correlation energy while dash-dot lines show the effects of polarization functions.

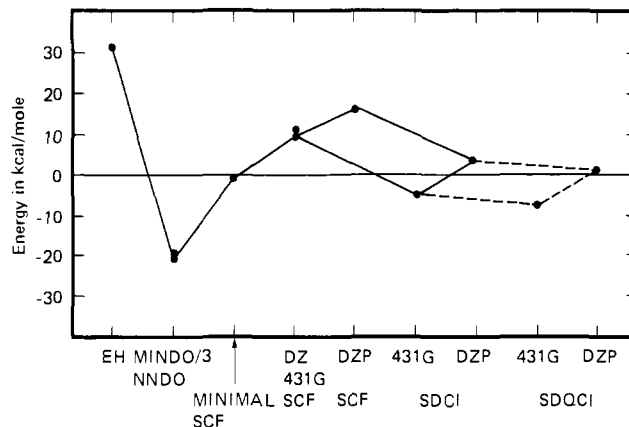
3. Estimates of correlation energy corrections due to quadrupole excitations given in these tables are obtained by using the Davidson formula.<sup>30</sup>

Table VI shows that the effects of polarization functions and correlation energy on the relative energies depend strongly on structures. For example, inclusion of polarization functions increases the relative energy of hydroxyacetylene by 3.4 kcal/mol while that of formylmethylene is decreased by 6 kcal/mol. Similarly, correlation energy corrections increase the relative energy of formylmethylene by 8.2 kcal/mol while that of oxirene is reduced by 5.2 kcal/mol. For formylmethylene, both effects are substantial but tend to cancel each other out. Consequently, the SCF(4-31G) wave function gives a reasonable result.

Comparison of the SD correlation energy corrections on the relative energies obtained with the 4-31G and DZ+P basis sets for oxirene (see Table VI) indicates that the SD corrections are in general converged to within 1.5 kcal/mol. For the other two isomers, the convergence is much better. Thus, the SD correlation corrections are relatively insensitive to the polarization functions.

There have been several calculations on the isomers of  $C_2H_2O$ , but only the recent calculation by Dykstra<sup>15</sup> is of accuracy comparable to ours. For hydroxyacetylene, Dykstra obtained relative energies of 34.3, 35.7, and 35.4 kcal/mol with SCF(DZ+P), SCEP(DZ+P), and SCEP(DZ+P)+quad, respectively. These results are in good agreement with ours, differences being less than 1 kcal/mol. The differences between Dykstra's SCF and SCEP results and ours are mainly due to differences in basis sets. Both calculations employed the same number of primitive and contracted Gaussian functions but differ in orbital exponents and the manner of contraction. Our basis gives and SCF energy of -151.76255 au for ketene while Dykstra's basis yields -151.75557 au. According to our results, only 0.001 au of this difference of 0.00668 au can be attributed to differences between geometries used in the two calculations. There is also a difference of about 0.003 au in the SD correlation energy in favor of our basis set.

However, Dykstra's and our results for the correlation corrections due to quadruple excitations show considerable disparities. For example, our estimate of this correction on the total energy of ketene is 0.04517 au while Dykstra's calculation yields 0.00185 au, suggesting that Dykstra's results are underestimated while our results are overestimated. For the relative energy of hydroxyacetylene, both calculations give a small value of 0.3 kcal/mol but different signs. For oxirene differences are more pronounced. Our result is -2.6 kcal/mol with the 4-31G basis



**Figure 4.** Relative energies of oxirene and formylmethylene,  $E(\text{oxirene}) - E(\text{formylmethylene})$ , as a function of degree of sophistication of methods used. A positive value means formylmethylene is more stable. The values for the extended Hückel MO(EH), MINDO/3, and NNDO methods and ab initio SCF method with a minimal basis set (MINIMAL SCF) and with a DZ basis set (DZ SCF) are compiled by Strausz et al. (ref 11). Others are from the present calculation.

**Table VII.** Calculated Dissociation Energies (kcal/mol)<sup>a</sup>

reactn no.	dissociatn	basis	SCF	SDCI	SDQCI
I	ketene $\rightarrow$ $CH_2(a^1A_1) + CO(X^1\Sigma^+)^b$	4-31G	83.6	97.6	104.5
		DZ+P	69.8	68.9	77.4
II	hydroxyacetylene $\rightarrow$ $C_2H(X^2\Sigma^+) + OH(X^2\Pi)$	4-31G	84.9	90.0	94.1
		DZ+P	94.7	100.9	109.7
III	oxirene $\rightarrow$ $C_2H_2(X^1\Sigma_g^+) + O(^1D)$	4-31G	13.8	39.2	48.7
		DZ+P	42.7	67.1	80.2

<sup>a</sup> Dissociated fragment energies were calculated for the experimental geometries except for  $C_2H$  where a CI optimized geometry (ref 31) was used. <sup>b</sup> The experimental dissociation energy  $D_0$  is 85.4 kcal/mol.<sup>32</sup>

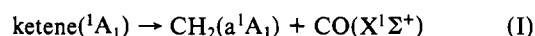
set whereas Dykstra obtained -0.6 kcal/mol with his DZ basis set. However, we may conclude from the above comparison that this correction is most likely less than 2 kcal/mol for oxirene and much less for the other two isomers. From the magnitude of the quadrupole corrections combined with the convergence pattern discussed above, we estimate the error in the SDCI(DZ+P) relative energy for oxirene to be  $\pm 2$  kcal/mol since the effect of polarization functions is small. For formylmethylene, the sum of the two effects is small and thus the above error estimate should be adequate. For hydroxyacetylene the correlation corrections are small, and we expect the effect of polarization functions to be converged to within  $\pm 2$  kcal/mol.

The relative stability of formylmethylene and oxirene has been studied extensively. Strausz et al.<sup>11</sup> have reviewed previous results and made a plot of this stability against the degree of sophistication of the methods, up to the SCF(DZ) results. We have extended this plot in Figure 4. The relative energy is defined as eq 2.

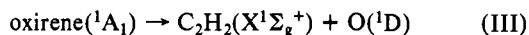
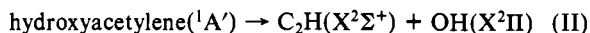
$$\Delta E = E(\text{oxirene}) - E(\text{formylmethylene}) \quad (2)$$

Therefore, a positive value means formylmethylene is more stable than oxirene. Although the semiempirical results tend to scatter, there are definite trends in the SCF and CI results. Improvement in the basis set stabilizes formylmethylene more than oxirene while the correlation energy correction has an opposite effect. It should be recalled, however, that in the SDCI calculation, with both 4-31G and DZ+P basis sets, formylmethylene is unstable with respect to rearrangement to ketene. Therefore, in Figure 4, we have used the energies calculated from the SCF optimized geometry in order to show the trends discussed above.

The thermodynamical stabilities of the isomers of  $C_2H_2O$  against possible dissociation products are also interesting. We have calculated dissociation energy  $D_e$  for reactions I-III. Results



(30) S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, **8**, 61 (1974).



are given in Table VII. Dissociated-fragment energies were calculated for the experimental geometry, except for  $\text{C}_2\text{H}$  where the CI optimized geometry was used.<sup>31</sup> The most recent experimental value of  $D_0$  for reaction I is  $85.4 \pm 0.3$  kcal/mol,<sup>32</sup> which should be compared with our SDQCI result of 77.4 kcal/mol. This comparison suggests that the errors in other SDQCI results are probably within  $\pm 10$  kcal/mol.  $D_e$  for reaction III is calculated to be 80 kcal/mol, of which the correlation and polarization contributions are 38 and 30 kcal/mol, respectively. We note that this calculated contribution is within the empirical estimate of 30–60 kcal/mol given by Strausz et al.<sup>11</sup> We also note that singlet oxirene is lower in energy than the dissociation limit  $\text{C}_2\text{H}_2(X^1\Sigma_g^+) + \text{O}(^3P)$  by 35 kcal/mol. For reaction II, the correlation and polarization contributions are relatively small, being 15 and 10 kcal/mol, respectively. The  $D_e$  of 110 kcal/mol indicates that the CO bond in hydroxyacetylene is stronger than the average single CO bond of 80 kcal/mol.

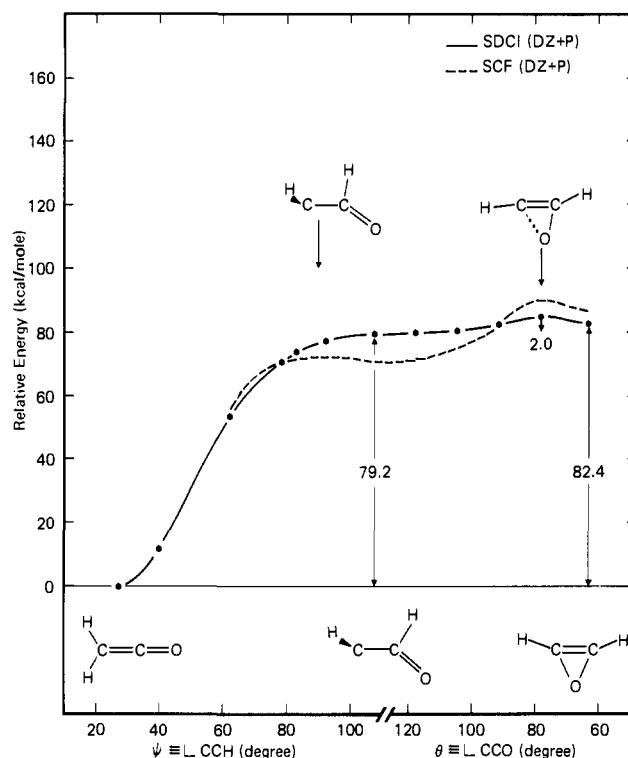
The main results of our energy determination of the isomers of  $\text{C}_2\text{H}_2\text{O}$  are summarized below. First, hydroxyacetylene is an energetically more accessible isomer than formylmethylene and oxirene. Second, the energy of oxirene relative to ketene is  $82 \pm 2$  kcal/mol, which is close to the energy of 85.4 kcal/mol for the dissociation of ketene to  $\text{CH}_2(^1A_1) + \text{CO}(X^1\Sigma^+)$ . Third, the effects of polarization functions and correlation energy on relative energies are significant and have a strong dependence on structure, but the two effects appear to be additive. Finally, the SDCI relative energies calculated at the SCF(DZ+P) and SDCI(DZ+P) optimized geometries are essentially the same, differences being less than 0.2 kcal/mol (see Table VI). We expect a similar situation also exists for rearrangement paths and their energy profiles.

### III. Rearrangement Paths and Activation Barriers

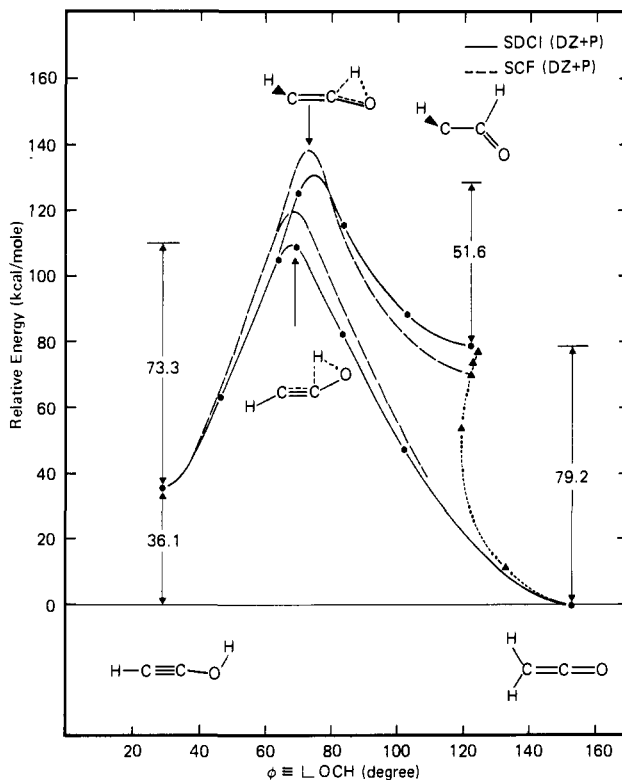
**A. Calculations.** A search for rearrangement paths between the isomers was done as follows. First, a potential surface which should include probable paths was mapped out in a coarse grid by using the SCF(4-31G) wave function. We then chose a reaction coordinate for each path and selected five values for each reaction coordinate in such a way that the entire path would be reasonably well presented. Each path was then determined first with the SCF(4-31G) wave function by relaxing all geometrical parameters except the reaction coordinate. We designate these paths as (4-31G) paths. These paths were refined by using the SCF(DZ+P) wave function, again with optimization of all geometrical parameters involved. The correlation correction on the energy profiles of the paths was estimated by the SDCI(DZ+P) calculation on the (DZ+P) path. Optimization of the paths using the SDCI(DZ+P) wave function was not done because results for the relative energies of the isomers of  $\text{C}_2\text{H}_2\text{O}$  indicated that the effect of geometry optimization on the energy profile would be very small ( $\sim 0.2$  kcal/mol).

**B. Rearrangement Paths and Their Energy Profiles.** We have investigated four rearrangement paths: path A, ketene  $\rightleftharpoons$  formylmethylene; path B, formylmethylene  $\rightleftharpoons$  oxirene; path C, ketene  $\rightleftharpoons$  hydroxyacetylene; path D, formylmethylene  $\rightleftharpoons$  hydroxyacetylene. The reaction coordinates selected are  $\angle\text{C}_1\text{C}_2\text{H}_2(\Psi)$  for path A,  $\angle\text{C}_1\text{C}_2\text{O}(\theta)$  for path B, and  $\angle\text{OC}_2\text{H}_2(\phi)$  for path C and D. These angles and other geometrical parameters are defined in Figure 2.

Table VIII lists geometrical parameters for the rearrangement paths calculated at the selected points with SCF(DZ+P) wave functions. The SCF(DZ+P) and SDCI(DZ+P) energies for these points are given relative to the corresponding energies for ketene. The energy profiles for paths A and B are shown in Figure 5 and



**Figure 5.** Energy profiles calculated with our DZ+P basis for the oxirene-formylmethylene rearrangement path along a reaction coordinate  $\theta \equiv \angle\text{C}_1\text{C}_2\text{O}$  and formylmethylene-ketene path along  $\Psi \equiv \angle\text{C}_1\text{C}_2\text{H}_2$ . For further details, see Table VIII.



**Figure 6.** Energy profiles calculated with our DZ+P basis for the hydroxyacetylene-formylmethylene and -ketene rearrangement paths along a reaction coordinate  $\phi \equiv \angle\text{OC}_2\text{H}_2$  (see Figure 2). An energy profile (solid triangles) for the formylmethylene-ketene path is also shown as a function of  $\phi$ . For further details, see Table VIII.

those for paths C and D in Figure 6.

Figure 5 clearly shows that path A has no barrier in the SDCI(DZ+P) approximation, although there is a small barrier of 0.9 kcal/mol in the SCF(DZ+P) approximation. This means

(31) V. Staemmler and A. D. McLean, to be submitted for publication.

(32) D. Feldmann, K. Meler, H. Zacharias, and K. H. Welge, *Chem. Phys. Lett.*, **59**, 171 (1978).

Table VIII. Geometrical Parameters and Relative Energies of Reaction Intermediates Along Various Isomerization Paths Optimized with the SCF(DZ+P) Wave Function

path	reaction coord, <sup>a</sup> deg			dist, Å				angles, deg		rel energy, <sup>b</sup> au	
	$\theta$	$\Psi$	$\phi$	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -O	C <sub>2</sub> -H <sub>2</sub>	C <sub>1</sub> -H <sub>1</sub>	$\alpha$	$\beta$	SCF	CI
oxirene	64.8	162.6	132.6	1.250	1.465	1.065	1.065	0.0	17.4	0.1388	0.1312
	77.8	150.9	131.3	1.248	1.357	1.072	1.062	0.0	3.7	0.1433	0.1343
	89.2	142.3	128.5	1.405	1.226	1.083	1.088	69.2	-8.1	0.1334	0.1320
	90.8	140.6	128.6	1.411	1.222	1.084	1.088	69.5	-9.8	0.1318	0.1316
	103.8	129.9	126.3	1.438	1.212	1.088	1.091	69.7	-14.5	0.1211	0.1280
formylmethylene	116.8	119.1	124.1	1.447	1.205	1.095	1.092	69.5	-5.8	0.1147	0.1265
	129.6	107.7	122.7	1.429	1.193	1.111	1.089	69.0	10.2	0.1131	0.1262
	142.9	93.0	124.1	1.400	1.188	1.139	1.091	68.9	21.0	0.1145	0.1234
	153.6	83.0	123.4	1.355	1.180	1.182	1.086	65.5	21.8	0.1140	0.1174
	159.8	78.0	122.2	1.323	1.176	1.214	1.082	62.5	17.7	0.1119	0.1122
ketene	179.2	61.9	118.9	1.239	1.176	1.384	1.060	0.0	-8.8	0.0887	0.0858
	186.7	40.2	133.1	1.280	1.149	1.769	1.064	0.0	-44.4	0.0186	0.0182
	180.0	27.1	152.9	1.309	1.147	2.056	1.073	0.0	-61.0	0.0	0.0
	202.7	54.7	102.6	1.256	1.177	1.426	1.056	0.0	-24.1	0.0814	0.0769
	216.7	59.7	83.6	1.239	1.214	1.274	1.058	0.0	-19.5	0.1422	0.1331
hydroxyacetylene	203.6	86.4	70.0	1.213	1.268	1.206	1.060	0.0	-5.3	0.1894	0.1743
	188.7	106.7	64.6	1.204	1.272	1.225	1.059	0.0	0.0	0.1859	0.1697
	181.4	133.0	45.6	1.188	1.279	1.508	1.058	0.0	0.0	0.1067	0.1016
	178.4	153.0	28.6	1.186	1.302	1.857	1.059	0.0	0.0	0.0559	0.0577
	181.4	133.0	45.6	1.188	1.279	1.058	1.058	0.0	0.0	0.1067	0.1016
formylmethylene	188.7	106.7	64.6	1.204	1.272	1.225	1.059	0.0	0.0	0.1859	0.1697
	164.8	125.2	70.0	1.363	1.261	1.148	1.082	62.2	20.5	0.2157	0.1992
	144.4	132.0	83.6	1.398	1.243	1.108	1.087	66.8	15.7	0.1787	0.1831
	135.7	121.7	102.6	1.424	1.241	1.105	1.091	69.2	9.6	0.1295	0.1411
	129.6	107.7	122.7	1.429	1.193	1.111	1.089	69.0	10.2	0.1131	0.1262

<sup>a</sup>  $\theta$  is used for the oxirene-formylmethylene path,  $\Psi$  for the formylmethylene-ketene path and  $\phi$  for the ketene-hydroxyacetylene-formylmethylene path. <sup>b</sup> For ketene total SCF and SDCI energies are -151.762 25 and -152.160 07 au, respectively.

formylmethylene is not a stable isomer; the hydrogen atoms can freely migrate from the formylmethylene position to the ketene position. We note that the reaction intermediates retain a formylmethylene-like structure until almost halfway to ketene. That is, although the reaction coordinates  $\Psi$  changes from 107.6° to 78°, the angles  $\phi$ ,  $\alpha$  and  $\beta$  are essentially unchanged (see Table VIII and Figure 6 where path A is plotted as a function of  $\phi$  instead of its reaction coordinate  $\Psi$ ).

Since formylmethylene is not stable, it is not possible to ascribe a structure to it. However, we shall use the SCF(DZ+P) structure and corresponding energy as those of formylmethylene in the discussions to follow. This is reasonable because the energy profile is relatively flat in the vicinity of this structure.

Path B has a small barrier. The barrier for the oxirene → formylmethylene (or ketene) reaction is calculated to be 2 kcal/mol. Thus, oxirene is a weakly bound isomer with respect to ring opening. Since there is no other path in the singlet surface with a lower barrier than this particular path, oxirene must isomerize to ketene through the formylmethylene structure.

It might be expected that the rearrangement path between ketene and hydroxyacetylene (path C) would pass through the formylmethylene-like structure. However, all points on path C correspond to planar symmetry. The transition state lies about 30 kcal/mol above formylmethylene and has a planar formylmethylene-like structure. The direct path between hydroxyacetylene and formylmethylene (path D) has a barrier higher than that of path C, and the transition state has a nonplanar formylmethylene-like structure. However, both paths have high enough barriers that hydroxyacetylene could not play any role in the Wolff rearrangement.

**C. Activation Barriers.** Barrier heights are estimated from the energy profiles, and results obtained in various approximations are listed in Table IX. The first column gives the SCF(4-31G) results obtained from the (4-31G) paths. The SCF(DZ) results obtained by other workers are given in the second column. A comparison of these two columns clearly shows that the (4-31G) basis yields essentially the same results as those of the (DZ) basis, differences being less than 2 kcal/mol. The third and fourth columns give the (DZ+P) results. The effects of polarization functions on barrier heights are substantial, as much as 18 kcal/mol, and vary significantly from path to path. The effects

Table IX. Activation Barriers (kcal/mol) for Interconversions of the Isomers, I to IV,<sup>a</sup> Calculated in Various Approximations

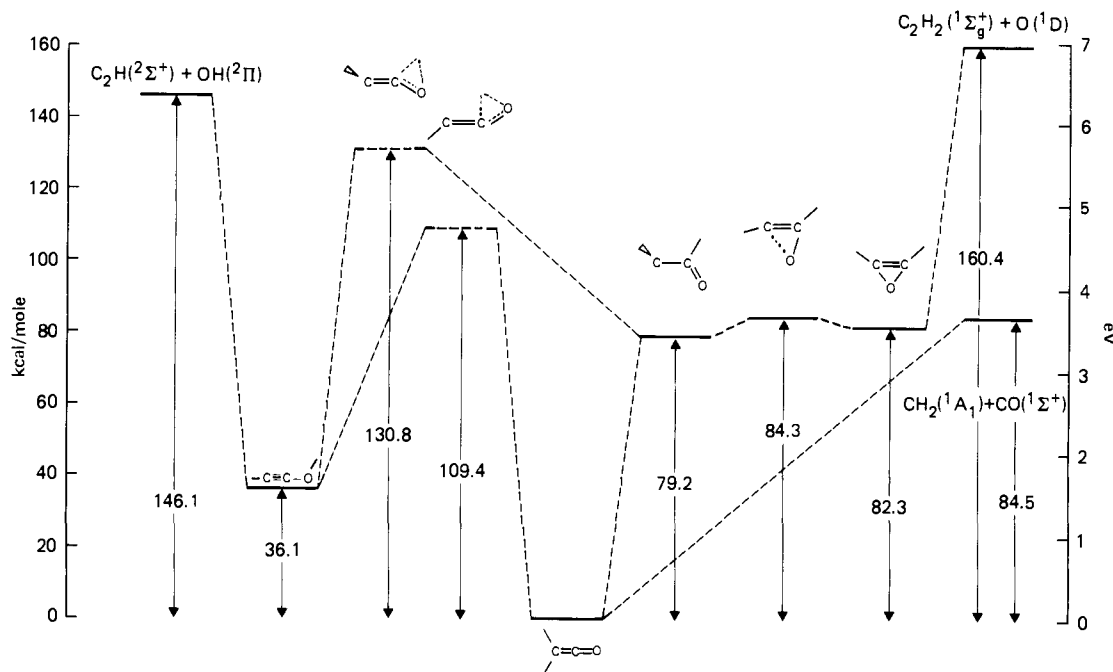
method	SCF	SCF <sup>b</sup>	SCF	SDCI	SDCI <sup>c</sup>
basis	4-31G	DZ	DZ+P	DZ+P	41-31G, DZ+P
path	4-31G	DZ	DZ+P	DZ+P	4-31G
I → III	81.2	80.0	71.9	79.2	80.5
III → I	4.2	5.7	0.9	0.0	0.0
III → IV	17.6	19.1	19.0	5.1	4.7
IV → III	6.1	7.3	2.8	2.0	1.2
I → II	126.8		119.0	109.4	108.8
II → I	95.0		83.9	73.2	72.5
II → III	95.2		103.9	94.6	94.4
III → II	50.0		67.6	51.6	50.6

<sup>a</sup> I = ketene, II = hydroxyacetylene, III = formylmethylene, and IV = oxirene. <sup>b</sup> Strausz et al.<sup>13</sup> <sup>c</sup> See the text for the method of calculation.

of correlation energy are also quite large, as much as 17 kcal/mol, but unlike the effects of polarization functions it appears to always lower the barrier.

As pointed out in section II, the effects of polarization and correlation appear to be additive. To confirm this additivity for barrier heights, we have carried out the following calculations: on the (4-31G) paths, SCF(DZ+P) calculations for the polarization effect and SDCI(4-31G) calculations for the correlation effect. The resulting energy profiles are used to estimate the barrier heights and the results are shown in the last column of Table IX. A good agreement with the SDCI(DZ+P) results is obtained, differences being less than 2 kcal/mol.

Calculations on triplet and excited singlet surfaces are in progress and will be reported elsewhere. Preliminary results, however, give the following indications. First, the lowest triplet and excited singlet states of oxirene are quite high in energy and lie respectively about 100 and 150 kcal/mol above the ketene ground state. While closed-shell singlet formylmethylene has nonplanar symmetry, triplet formylmethylene has planar symmetry. It lies about 60 kcal/mol above ketene and 20 kcal/mol below singlet formylmethylene. At the triplet formylmethylene geometry, the closed-shell <sup>1</sup>A' and open-shell <sup>1</sup>A'' lie respectively about 50 and 20 kcal/mol above the <sup>3</sup>A'' state. This suggests that the lowest excited singlet potential surface may cross the singlet



**Figure 7.** Relative energies of the  $C_2H_2O$  isomers, activated complexes, and dissociated fragments. For the isomers and complexes the SDCI(DZ+P) results are given, and for the dissociated fragments the SDQCI(DZ+P) results are shown except for the  $CH_2(1A_1) + CO(1\Sigma^+)$  system where the observed value taken from ref 32 is used.

ground-state (closed-shell) potential surface in the vicinity of the closed-shell singlet formylmethylene structure and the energy at the crossing would be close to that of singlet formylmethylene.

We have also carried out SCF(4-31G) calculations on the structure and energy of the ground state of diazoethanone. The results indicate that the  $C_2H_2O$  group of diazoethanone has a geometry essentially similar (bond length within 0.02 Å) to that of formylmethylene, the only difference being that diazoethanone is planar. The decomposition of diazoethanone into formylmethylene and nitrogen is calculated to be endoergic by about 30 kcal/mol. Csizmadia et al.<sup>18</sup> has estimated this energy to be 35 kcal/mol with the use of the extended Hückel method, which is reasonable agreement with our results.

The results on energy differences and barrier heights, summarized in Figure 7, and the preliminary results presented above lead to the following observations. Since the relative energy of the lowest excited state of oxirene is much higher than the photon energy employed in the photolysis of  $^{14}CH_2CO$  (85.6–91.4 kcal/mol),<sup>7</sup> scrambling of  $^{14}C$  must take place on the ground state of the  $C_2H_2O$  system. A barrier height of 84 kcal/mol for the ketene–oxirene rearrangement is also in accord with the observation that considerably less scrambling take place in high-pressure than low-pressure experiments<sup>7</sup> due to collisional deactivation at high pressures. This also implies the absence of a significant barrier in the path from ketene to formylmethylene on the lowest excited singlet surface.

The thermal decomposition of diazoethanone most likely proceeds exclusively on the ground-state surface. This is especially probable because of the similar geometries of diazoethanone and formylmethylene. The latter, once formed in its ground state by either thermolysis or photolysis, rearranges without activation barrier into ketene. The lack of a barrier to rearrangement of formylmethylene into ketene explains the failure of Krantz<sup>9</sup> to observe anything but ketene during matrix isolation studies of the diazoethanone photolysis at temperatures as low as 8 K. Scrambling of isotopically labeled diazoethanone during photochemical decomposition must also occur on the ground-state surface of  $C_2H_2O$  because the lowest singlet excited state of oxirene lies 150 kcal/mol above the ground state of ketene. Because of

the energy barrier in the oxirene  $\rightleftharpoons$  formylmethylene path, the amount of carbon scrambling and thus oxirene participation should reflect the excess vibrational energy and thus depend upon the temperature, as has been demonstrated for higher homologues of diazoethanone by Matlin and Sammes.<sup>6</sup>

#### IV. Conclusions

From the results discussed above, we draw the following conclusions about the mechanism of the Wolff rearrangement (WR) of diazoethanone.

(1) Hydroxyacetylene does not play a role in the WR due to high energy barriers.

(2) Formylmethylene is not a stable isomer. This explains the absence of experimental evidence of its participation in the WR.

(3) Oxirene is certainly not a long-lived intermediate. The energy barrier for rearrangement to ketene is very small, explaining why oxirene has not been isolated experimentally.

(4) The thermal WR occurs on the ground state surface of the  $C_2H_2O$  system, and the amount of carbon scrambling depends on the amount of vibrational energy available.

(5) In the photochemical WR of diazoethanone and also in the photolysis of ketene, carbon scrambling occurs on the ground state surface of the  $C_2H_2O$  system.

We note that these conclusions have been inferred from experimental observations<sup>7,9</sup> and from theoretical calculations.<sup>11–18</sup> We believe, however, that our calculations are sufficiently accurate to provide a firm basis for these conclusions.

Potential surfaces pertinent to the WR of other diazoketones may differ in some details, but the main features should remain similar to those of diazoethanone—in particular that the Wolff rearrangement is an energetically down hill, unimpeded process on the ground singlet surface. Thus, the conclusions stated above should in general be applicable to other diazoketones.

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