

The structure of gaseous biacetyl was determined, at 225 and 525 °C, by using gas electron diffraction.<sup>26</sup> The results agree with those reported here: (1) the configuration of the gaseous molecule is only trans; (2) the C=O bond distance (1.215 Å) is within one standard deviation from the value found by us in the solid; (3) the central C—C distance is found to be longer than the C—C(methyl) distance, by 0.014 Å at 225 °C and by 0.028

Å at 525 °C. In the structure of the solid the difference is 0.064 Å, but again, as pointed out above, the foreshortening of the C—C(methyl) distance in the solid may tend to exaggerate this difference.

Registry No. 2,3-Butanedione, 431-03-8.

**Supplementary Material Available:** Tables 5 and 6 listing  $F_0$  and  $F_c$  at both temperatures (7 pages). Ordering information is given on any current masthead page.

(26) Danielson, D. D.; Hedberg, K. J. *Am. Chem. Soc.* 1979, 101, 3730.

## An Experimental and ab Initio Study of the Addition of Atomic Carbon to Water

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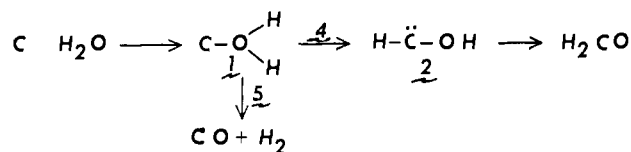
**Abstract:** Experimental and theoretical investigations of the reaction of atomic carbon with H<sub>2</sub>O were carried out and the results compared. The theoretical study, in which all geometries were optimized at 3-21G level and single point calculations performed at the UMP3/6-31G\*\* level, involved both <sup>1</sup>D and <sup>3</sup>P states of carbon. For C(<sup>1</sup>D) atoms, the process having the lowest activation enthalpy is cleavage of an initially formed carbon–water complex to CO and H<sub>2</sub> along a closed-shell surface ( $\Delta H^\ddagger = 5.2$  kcal/mol). Rearrangement of the closed-shell carbon–water complex to hydroxymethylene has  $\Delta H^\ddagger = 11.6$  kcal/mol. In the case of triplet carbon, the most favorable reaction of the initial carbon–water complex was simply dissociation to C + H<sub>2</sub>O. The  $\Delta H^\ddagger$  for rearrangement of the C(<sup>3</sup>P)–H<sub>2</sub>O complex to hydroxymethylene was 22.8 kcal/mol while the corresponding barrier for an open-shell singlet complex was 18.0 kcal/mol. The barrier to rearrangement of singlet hydroxymethylene to formaldehyde (38.9 kcal/mol) and that of triplet hydroxymethylene (41.3 kcal/mol) were similar. The experimental results were in agreement with theoretical predictions. Atomic carbon, generated by the thermolysis of 5-diazotetrazole, reacts with water to give carbon monoxide (9.5%) and formaldehyde (2.4%). Addition of O<sub>2</sub>, a scavenger of C(<sup>3</sup>P), increases the CO yield to 53.7% while leaving the formaldehyde yield unchanged. Reaction of carbon with O<sub>2</sub> alone produces only CO (47%). These results indicate that the state of carbon reactive toward water is a singlet, as indicated by the calculations.

Over the past several years it has become possible to apply ab initio methods to the study of potential energy surfaces with the thoroughness heretofore reserved for semiempirical methods. In particular, it is now feasible to obtain accurate ab initio predictions of reaction mechanisms and compare these predictions with experimentally observed pathways. In this paper we have utilized this approach to investigate the reaction between atomic carbon and water both experimentally and theoretically.

A study of the rather simple reaction of carbon with water is advantageous from both an experimental and a theoretical viewpoint. The fact that there are only four atoms involved in this system reduces the time required for computations and limits the number of product-forming steps that the experimentalist need consider.

Since there is little doubt that initial attack of carbon on water will occur at oxygen, we may formulate the pathways shown in Scheme I.<sup>1</sup> Both deoxygenation (via transition state 5) and O–H insertion (via transition state 4) have been observed in the reaction of carbon atoms with alcohols.<sup>2</sup> This paper will describe the energetics of the formation and subsequent reactions of the carbon–water complex, 1, the effect of the electronic state of carbon on the reaction, and the relative contributions of the reaction pathways in Scheme I.

Scheme I



Previous reports of the use of MO methods to study the reactions of atomic carbon have been limited to reactions with hydrogen,<sup>3</sup> ethylene,<sup>4</sup> oxirane,<sup>5</sup> and carbonyl compounds.<sup>6</sup>

### Method of Calculation

All stationary points have been located by using the GAUSSIAN80 program package<sup>7</sup> with no constraints except for symmetry when appropriate. The 3-21G basis set,<sup>8</sup> which has been shown to give results nearly identical with larger basis sets, is used to determine geometries. The geometries have been optimized by using analytical derivatives, and transition states have been located by finding a stationary point that has a developing negative eigenvalue

(1) For recent reviews of the chemistry of atomic carbon see: (a) Skell, P. S.; Havel, J.; McGlinchey, M. J. *Acc. Chem. Res.* 1973, 6, 97-105. (b) Mackay, C. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1-42. (c) Shevlin, P. B. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. I, pp 1-36.

(2) Skell, P. S.; Harris, R. F. *J. Am. Chem. Soc.* 1969, 91, 4440.

(3) Blint, R. J.; Newton, M. D. *Chem. Phys. Lett.* 1975, 32, 178.

(4) Dewar, M. J. S.; Haselback, E.; Shanshal, M. *J. Am. Chem. Soc.* 1970, 92, 3505.

(5) Figueroa, J. M.; Shevlin, P. B.; Worley, S. D. *J. Am. Chem. Soc.* 1976, 98, 3820.

(6) Dewar, M. J. S.; Nelson, D. J.; Shevlin, P. B.; Biesiada, K. A. *J. Am. Chem. Soc.* 1981, 103, 2802.

(7) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. "GAUSSIAN 80", QCPE 406, Indiana University, the version used here has been developed in other laboratories to run on an IBM machine.

(8) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, 102, 939.

in the updated matrix of second derivatives during optimization.<sup>9</sup> Although not definitive, by careful inspection of this eigenvalue one can give some confidence to its identification as a transition state.

Relative energies of geometry optimized species are calculated at the MP3/6-31G\*\* level<sup>10-12</sup> for closed-shell species and at the UMP3/6-31G\*\* level for open shells. Some of the geometries were taken from the Carnegie-Mellon Quantum Chemistry Archive.<sup>13</sup> For the sake of consistency, the optimized 3-21G geometries were used even when better ones (6-31G\*) were available.

Several force constant calculations have been performed by use of the HONDO molecular orbital package<sup>14</sup> in order to estimate zero point corrections at the 3-21G level as well as to confirm the identification of transition states.

Recent results<sup>15</sup> have shown that the relative energies of stationary points differ by less than 1 kcal/mol when large correlated basis sets are used on geometries optimized with or without explicit inclusion of correlation. This small difference, when compared to the 10–30 kcal/mol difference in going from a DZ basis to a polarized and correlated basis set, points out the general feature that, when resources are limited, computational effort is best spent on sophisticated single point calculations on reasonable geometries.

### Experimental Section

**Reaction of Atomic Carbon with Water.** Carbon atoms were generated by the thermolysis of 5-diazotetrazole<sup>16</sup> and reacted with water vapor. In a typical reaction, water vapor (1.0 mmol) was introduced into the flask containing diazotetrazole (0.1 mmol). The flask was then heated in an oil bath at 100 °C for about 3 min to decompose the tetrazole. The volatile products formed were passed first through a trap containing a suspension of excess dimedone<sup>17</sup> in 5% acetic acid at -196 °C and then through a trap containing charcoal at -196 °C to absorb carbon monoxide and nitrogen. Carbon monoxide and nitrogen were then analyzed by gas chromatography (GC) with a molecular sieve column. The first trap containing the product mixture, nonvolatile at -196 °C, along with dimedone was warmed to room temperature and heated at a temperature of 60–70 °C for 0.5 h. The product mixture was then evaporated to dryness under vacuum and the dried product dissolved in chloroform. The chloroform solution of the dimedone derivative of formaldehyde was analyzed by GC on a 6 ft SE-30 on Chromosorb WHP column.<sup>17</sup> Products and yields are shown in Table VII.

**Reaction of Atomic Carbon with Water in the Presence of Oxygen.** The reaction was carried out as described above with a mixture of oxygen (0.11 mmol) and water vapor (1.0 mmol) and gave the yields in Table VII.

### Theoretical Results

Atomic carbon exists in three low-lying electronic states. The most stable configuration is the <sup>3</sup>P followed by the <sup>1</sup>D 30 kcal higher in energy and the <sup>1</sup>S 62 kcal higher than the triplet.<sup>18</sup> Since there is unlikely to be sufficient energy for the production of electronically excited C(<sup>1</sup>S) under the experimental conditions, we have neglected this species in our calculations.

The energy of C(<sup>3</sup>P) was calculated at the UMP3/6-31G\*\* level by assuming unpaired electrons in two p orbitals. This procedure leads to a calculated  $\Delta H$  for the reaction  $C + H_2O \rightarrow CH_2O$  of -139.2 kcal/mol, which may be compared to an experimental value of -136.6 kcal/mol. The fact that C(<sup>1</sup>D) is composed of both open- and closed-shell configurations makes calculation of the energy of this species by the present method

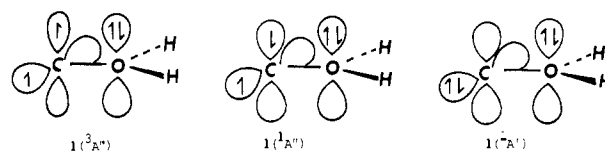
Table I. Energies (UMP3/6-31G\*\*) Relative to C(<sup>3</sup>P) + H<sub>2</sub>O and C(<sup>1</sup>D) + H<sub>2</sub>O (C(<sup>1</sup>D) Is Assumed to be 30.0 kcal Less Stable Than C(<sup>3</sup>P))

structure	energy <sup>a</sup>		
	C( <sup>3</sup> P), 113.97197 hartrees	C( <sup>1</sup> D), 113.92416 hartrees	
		closed shell	open shell
1	-6.4 ( <sup>3</sup> A'')	4.6 ( <sup>1</sup> A')	-20.1 ( <sup>1</sup> A'')
4	16.4	16.1	-2.1
5	34.3	9.8	4.3 <sup>b</sup>
2	-59.5 ( <sup>3</sup> A'')	-111.2 ( <sup>1</sup> A')	-71.0 ( <sup>1</sup> A'')
3	c	-166.6	c
CO + H <sub>2</sub>	c	-161.5	c

<sup>a</sup> Energies given in kcal/mol except where noted. <sup>b</sup> The transition state could not be located precisely. The barrier was calculated by assuming that the transition state had the same total energy as the triplet transition state. <sup>c</sup> Not calculated.

difficult. The energy of an open-shell singlet carbon is calculated to be 17.1 kcal higher than C(<sup>3</sup>P) at the UMP3/6-31G\*\* level, while a closed shell singlet carbon is 46.3 kcal higher than C(<sup>3</sup>P). Since the actual energy of C(<sup>1</sup>D) is between these values, we have used the experimental C(<sup>1</sup>D)–C(<sup>3</sup>P) energy difference of 30.0 kcal to determine the energy of C(<sup>1</sup>D).

**Carbon–Water Complex 1.** Three different electronic states of **1**, <sup>3</sup>A'', <sup>1</sup>A'', and <sup>1</sup>A', were considered for the initial collision complex between carbon and water. A state correlation diagram



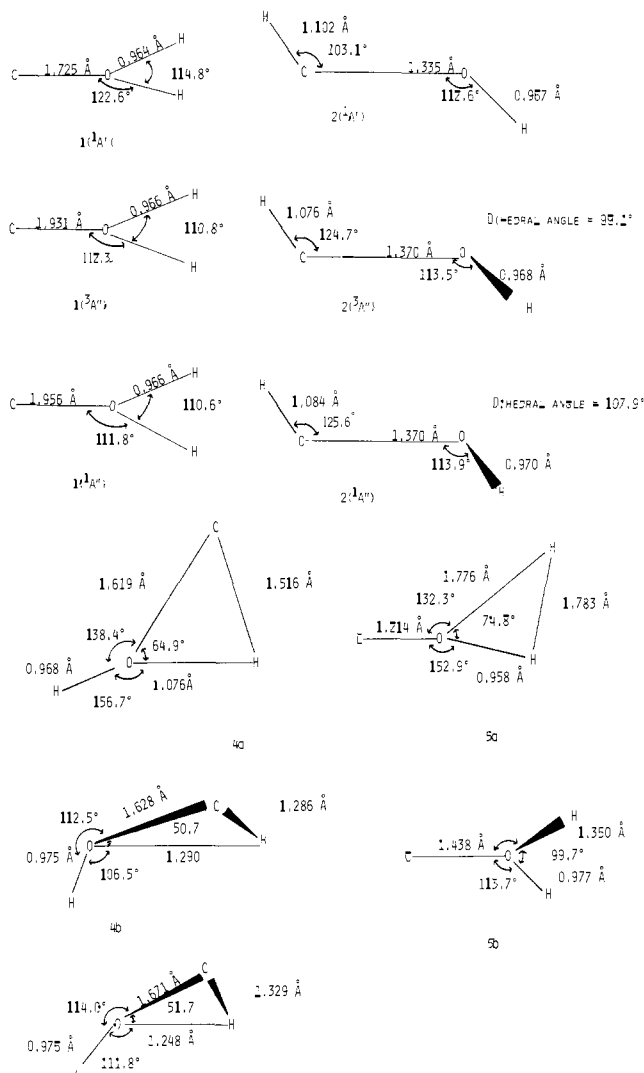
shows that C(<sup>3</sup>P) correlates with **1**(<sup>3</sup>A'') and that C(<sup>1</sup>D) correlates with both the open-shell (<sup>1</sup>A'') and closed-shell (<sup>1</sup>A') singlet states of **1**.<sup>19</sup> Hence, we have calculated the reaction coordinate for  $C + H_2O$  on both open- and closed-shell singlet surfaces and on the triplet surface. Table I presents energies calculated for various intermediates and transition states in Scheme I relative to carbon, in a particular electronic state, and water. Thus, the first column of energies is relative to H<sub>2</sub>O and C(<sup>3</sup>P) while the next two columns relate to H<sub>2</sub>O and C(<sup>1</sup>D) on closed- and open-shell surfaces respectively.

The triplet complex **1**(<sup>3</sup>A'') is calculated to lie 6.4 kcal/mol lower in energy than C(<sup>3</sup>P) + H<sub>2</sub>O and is the most stable of the three electronic states of **1**. The open-shell complex **1**(<sup>1</sup>A'') is 20.1 kcal/mol more stable than C(<sup>1</sup>D) + H<sub>2</sub>O (<sup>3</sup>A'' – <sup>1</sup>A'' = 16.3 kcal/mol). The closed-shell complex **1**(<sup>1</sup>A') is predicted to be an energy minimum with respect to a closed-shell C atom + H<sub>2</sub>O. However, since a closed-shell C atom is not a good approximation of C(<sup>1</sup>D), this minimum, which is calculated at 24.7 kcal/mole above **1**(<sup>1</sup>A''), may be an artifact. The geometries of **1**, **2**, **4**, and **5** used in these calculations are shown in Figure 1.

The complexes **1**(<sup>3</sup>A'') and **1**(<sup>1</sup>A'') are similar and will be discussed together. For both spin states, there are two mutually perpendicular singularly occupied orbitals. For the triplet complex, both orbitals contain electrons of the same spin while in the singlet complex the electrons have opposite spin. In the triplet, there is no net stabilization for the  $\alpha$  spin electrons as all interactions involved occupied orbitals and hence stabilization of one orbital results in the destabilization of another. For the  $\beta$  spin electrons, however, two interactions yield net stabilization. Both the b<sub>1</sub> and b<sub>2</sub> orbitals on H<sub>2</sub>O can interact with an empty (no other  $\beta$  electron) orbital on carbon. The stabilization of the singlet complex involves an  $\alpha$  spin electron in the b<sub>1</sub> orbital of H<sub>2</sub>O interacting with a vacant

- (9) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.  
 (10) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.  
 (11) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.  
 (12) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.  
 (13) Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon University, Pittsburgh, PA, 1981.  
 (14) Dupuis, M.; Rys, J.; King, H. R. *J. Chem. Phys.* **1976**, *65*, 111.  
 (15) Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394.  
 (16) Dyer, S. F.; Shevlin, P. B. *J. Am. Chem. Soc.* **1979**, *101*, 1303.  
 (17) János, É.; Balla, J.; Tyihák, E.; Gáborjányi, R. *J. Chromatogr.* **1980**, *191*, 239.  
 (18) Moore, C. E. "Atomic Energy Levels" *Natl. Bur. Stand. (U.S.) Circ.* **1949**, *1*, No. 467.

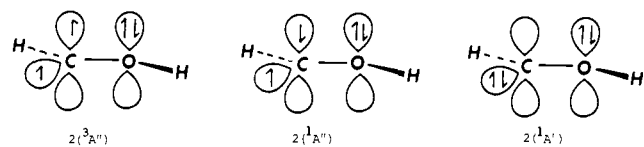
(19) A correlation diagram connecting the states of  $C + H_2O$  with those of  $CO + H_2$  and  $CH + OH$  has been presented by: Husain D.; Newton, D. P. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 51. Although this treatment did not include the initial complex **1**, it is clear that C(<sup>1</sup>D) correlates with both **1**(<sup>1</sup>A') and **1**(<sup>1</sup>A'') and that C(<sup>1</sup>S) correlates with a higher closed-shell electronic state of **1**.



**Figure 1.** Geometries calculated for various intermediates and transition states in the reaction of carbon with water.

orbital (no other  $\alpha$  electron) on carbon and a  $\beta$  electron in the  $b_2$  orbital interacting with the perpendicular vacant orbital (no other  $\beta$  electron) on carbon. The fact that there are no orientations of the open-shell complexes that avoid repulsions between the electrons in a singularly occupied orbital on carbon and an oxygen lone pair may account for the longer C–O bond lengths in  $1(3A'')$  and  $1(1A'')$  as compared to  $1(1A')$ . While the  $1A'$  complex is planar, the  $3A''$  and  $1A''$  complexes are pyramidal (sum of angles:  $3A'' = 335^\circ$ ;  $1A'' = 334^\circ$ ).

**The Rearrangement of Complex 1 to Hydroxymethylene, 2.** According to Hammond's postulate,<sup>20</sup> the transition state for rearrangement of **1** to **2** is predicted to be early, due to the large exothermicity of the reaction. Thus, the calculated transition state, **4a**, for the rearrangement of  $1(1A')$  to  $2(1A')$  has a short O–H



distance for incipient bond breaking (1.076 Å) and a long distance for the forming C–H bond (1.516 Å). The C–O bond has shortened by 0.105 Å in the transition state but is still "reactant like". The formation of  $2(1A')$  from  $C(1D) + H_2O$  is predicted to have a barrier of 16.4 kcal/mol. The fact that  $1(3A'')$  and

**Table II.** Vibrational Frequencies ( $\text{cm}^{-1}$ ) Obtained for Complex  $1(1A')$  and Transition State **5a** (Scheme I)

$1(1A')$		<b>5a</b>	
294	OH <sub>2</sub> wag	1468i	OH <sub>2</sub> scissor
416	CO stretch	384	OH <sub>2</sub> wag
684	OH <sub>2</sub> rock	702	OH <sub>2</sub> stretch
1741	OH <sub>2</sub> scissor	1184	OH stretch
3821	OH <sub>2</sub> sym stretch	1604	CO stretch
3974	OH <sub>2</sub> asym stretch	3937	OH stretch

$1(1A'')$  are nonplanar due to lone pair–lone electron repulsions also manifests itself in the rearrangement of  $1(3A'')$  and  $1(1A'')$  to  $2(3A'')$  and  $2(1A'')$ . Hydrogen transfer in the molecular plane is 13.4 kcal/mol higher in energy than the nonplanar transition state (**4b**) for rearrangement of  $1(3A'')$  and 10.8 kcal/mol higher for the in-plane compared to the out-of-plane transition state (**4c**) for rearrangement of  $1(1A'')$ . The transition states are also interesting in terms of orbital correlations. In the singlet, the hydrogen is transferred to the orbital containing the lone pair on carbon that is in the molecular plane. However, in the triplet, the singly occupied orbital nearly perpendicular to the pseudo molecular plane accepts the hydrogen. The nonplanar barrier to rearrangement of  $1(3A'')$  to  $2(3A'')$  is 22.8 kcal/mol and that for rearrangement of  $1(1A'')$  to  $2(1A'')$  is 18.0 kcal/mol.

**Elimination of Hydrogen from 1.** An examination of the pathway for elimination of hydrogen from **1** revealed the large differences in barrier heights with change in electronic states shown in Table I. For the closed-shell energy surface the only transition state that could be found was the asymmetric elimination of H<sub>2</sub>. This transition state, **5a**, is similar in character to that found by other workers<sup>15,21,22</sup> for the elimination of H<sub>2</sub> from formaldehyde. However, the predicted barrier from  $1(1A')$  of 5.2 kcal/mol is much lower in the present case and reflects the large exothermicity of the reaction. A similar pathway is not available to the triplet due to very high triplet energies for CO or H<sub>2</sub>. Instead, the preferred mode, **5b**, is simply an O–H fission in which it is clear that, for the triplet to correlate with two doublets (COH + H), a HOMO–LUMO crossing must occur. As the O–H bond is stretched, there is a crossing from the highest occupied MO (single electron on carbon) to an orbital that is mainly localized on the departing hydrogen. This crossing leads to a barrier of 40.7 kcal/mol for the triplet. Problems with convergence prevented the transition state for loss of hydrogen from  $1(1A'')$  from being located precisely, but the partially converged transition state suggests a mechanism similar to that of the triplet at the 3-21G level. Thus, we have the interesting conclusion that the closed-shell surface leads to CO + H<sub>2</sub> while the open-shell complexes,  $1(3A'')$  and  $1(1A'')$ , rearrange to hydroxymethylene. It may be of interest to note that a very sophisticated calculation on COH predicts that the barrier to loss of H is 18 kcal/mol.<sup>23</sup> This value is lower than the barrier to rearrangement of COH to HCO even though HCO is 40 kcal/mol more stable than COH.

Force constants were calculated for the closed-shell complex,  $1(1A')$ , and the transition state for its loss of hydrogen. The calculated frequencies and approximate assignments are given in Table II. These data lead to a calculated zero point energy for complex  $1(1A')$  of 15.6 kcal/mol and of 11.2 kcal/mol for the transition state (leaving out the imaginary frequency). Thus, the calculated barrier to loss of H<sub>2</sub> from  $1(1A')$  of 5.2 kcal/mol should be reduced by the difference (4.4 kcal/mol) to be a predicted value of 0.8 kcal/mol, giving a barrier of 5.4 kcal/mol for the production of CO and H<sub>2</sub> from  $C(1D) + H_2O$  on the closed-shell surface.

**Hydroxymethylene (2).** The carbene structure was optimized for all three electronic states at the 3-21G level. The relative energies at the UMP3/6-31G\*\* level indicate that the triplet is 21.7 kcal/mol less stable than the closed-shell singlet, and the

(20) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(21) Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F., III *J. Chem. Phys.* **1981**, *75*, 3459.

(22) Adams, G. F.; Bent, G. D.; Bartlett, R. J.; Purvis, G. D. *J. Chem. Phys.* **1981**, *75*, 834.

(23) Dunning, T. H. Jr. *J. Chem. Phys.* **1980**, *73*, 2304.

Table III. Geometries of Singlet Hydroxymethylene (2)<sup>a</sup>

method	r(C-O)	r(C-H)	r(O-H)	∠HCO	∠HOC	ref
3-21G	1.335	1.102	0.967	103.1	112.6	this work
MP2/6-31G*	1.323	1.113	0.978	101.4	107.2	b
DZP + P	1.320	1.112	0.964	101.9	108.0	c

<sup>a</sup> Bond lengths in Å; angles in deg. <sup>b</sup> Reference 15. <sup>c</sup> Reference 20.

Table IV. Calculated Barrier Heights (kcal/mol) for the Rearrangement of 2 to Formaldehyde

forward	reverse	method	ref
38.9	94.2	MP3/6-31G**// 3-21G	this work
39.1	93.6	MP3/6-31G**// MP2/6-31G*	a
35.8 (31.5)	90.7 (86.2)	MP4/6-31G**// MP2/6-31G*(ZPC) <sup>b</sup>	a
	(79.6)	MP4/(SDTQ)/ 6-311G**(ZPC) <sup>b</sup>	c
40.8	92.4		d
	90.4		e

<sup>a</sup> Reference 15. <sup>b</sup> Zero point correction included. <sup>c</sup> Reference 25. <sup>d</sup> Reference 21. <sup>e</sup> Reference 22.

open-shell singlet is 40.2 kcal/mol above the ground state. While the closed-shell singlet is much more stable, the <sup>3</sup>A'' and <sup>1</sup>A'' hydroxymethylenes maintain approximately the same energy separation as in the water-carbon complexes (**1**(<sup>3</sup>A'') - **1**(<sup>1</sup>A'') = 16.3 kcal/mol; **2**(<sup>3</sup>A'') - **2**(<sup>1</sup>A'') = 18.5 kcal/mol). Since the same orbitals remain occupied, this is not an unexpected result, and the two potential surfaces remain closely parallel at all points investigated. The geometry of the ground state singlet hydroxymethylene calculated at the 3-21G level is similar to that calculated by other methods, as shown in Table III. When the 3-21G geometry is used to compute a total energy at the MP3/6-31G\*\* level, the structure is 0.8 kcal/mol less stable than that corresponding to the MP2/6-31G\* geometry.<sup>15</sup>

A recent experimental determination of the enthalpy of formation of singlet hydroxymethylene<sup>24</sup> indicates that this species lies 54.2 kcal/mol above formaldehyde. This compares to a relative energy of 55.4 kcal/mol calculated at the MP3/6-31G\*\* level. On the other hand, triplet hydroxymethylene is only 4.8 kcal/mol less stable than triplet formaldehyde at the same level.

**Crossing of Triplet to Singlet Hydroxymethylene.** Intersystem crossing may be rapid from the triplet hydroxymethylene to the singlet. The closed-shell singlet hydroxymethylene is 21.7 kcal/mol more stable than the triplet. The potential well that holds the triplet is shallow compared to that of the singlet, and a distortion of the triplet geometry to the optimized singlet geometry increases the energy by only 7.4 kcal/mol. This suggests that the two vibronic wave functions are likely to overlap, which would increase the crossing rate.

**Rearrangement of Hydroxymethylene to Formaldehyde.** Table IV lists calculated barrier heights for rearrangement of hydroxymethylene, **2**, to formaldehyde that have been reported and provides a basis for comparison of our results with those obtained by other methods. One can easily see from the comparison with the work of Pople and co-workers<sup>15</sup> that the approximation of using 3-21G geometries rather than those obtained with correlation and polarization produces a smaller difference than the change in going from the MP3 method to the MP4 method.

The geometry parameters of the transition state for rearrangement of **2** to formaldehyde (Table V) are similar for all levels but not identical. The relative energies at the MP3/6-31G\*\* level do not seem to be sensitive to the differences in the method of calculating the geometry. The difference between the geometry obtained at the 3-21G level and that obtained with polarization

Table V. Geometric Parameters<sup>a</sup> of the Transition State for Rearrangement of 2 to Formaldehyde

method	R <sub>1</sub> , Å	R <sub>2</sub> , Å	S, Å	σ, deg	β, deg	ref
3-21G	1.247	1.089	1.312	55.9	116.6	this work
SCF	1.213	1.095	1.266	56.4	116.6	b
DZ + P	1.262	1.087	1.316	55.0	117.3	b
6-31G*	1.219	1.095	1.270	65.3	115.9	c
MP2/6-31G*	1.276	1.111	1.322	52.9	112.9	c

<sup>a</sup> See structure 6 for definition of parameters. <sup>b</sup> Reference 21. <sup>c</sup> Reference 15.

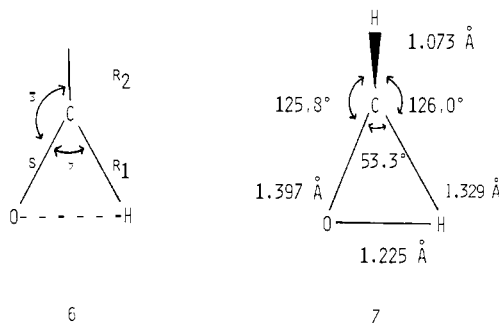
Table VI. Total Energies (-hartrees) for Molecular Species Represented in Scheme I

molecule	basis			
	3-21G	6-31G**	MP2/ 6-31G** <sup>a</sup>	MP3/ 6-31G** <sup>a</sup>
C( <sup>3</sup> P) + H <sub>2</sub> O	113.06703	113.70315	113.95229	113.97197
C( <sup>1</sup> D) + H <sub>2</sub> O				113.92416 <sup>b</sup>
C · · OH <sub>2</sub> ( <sup>1</sup> A')	113.00595	113.61795	113.89795	113.91686
C · · OH <sub>2</sub> ( <sup>3</sup> A'')	113.08768	113.70652	113.96568	113.98214
C · · OH <sub>2</sub> ( <sup>1</sup> A'')	113.05623	113.68068	113.93867	113.95615
HCOH ( <sup>1</sup> A')	113.14629	113.78935	114.08828	114.10141
HCOH ( <sup>3</sup> A'')	113.14372	113.78134	114.05408	114.06687
HCOH ( <sup>1</sup> A'')	113.10265	113.74293	114.02296	114.03724
O=CH <sub>2</sub> ( <sup>1</sup> A')	113.22182	113.68068	114.18279	114.18962
O=CH <sub>2</sub> ( <sup>3</sup> A'')	113.16642	113.79664	114.05309	114.07446
(CHO)H ( <sup>1</sup> A')	112.96248	113.58024	113.88606	113.89841
(CHO)H ( <sup>3</sup> A'')	113.01732	113.64456	113.93549	113.94579
(CHO)H ( <sup>1</sup> A'')	112.99629	113.62540	113.91642	113.92750
CO(H <sub>2</sub> ) ( <sup>1</sup> A')	112.91931	113.56148	113.90264	113.90856
COH(H) ( <sup>3</sup> A'')	113.00264	113.62245	113.90747	113.91728
H(CHC) ( <sup>1</sup> A')	113.05005	113.70655	114.04046	114.03944
H(CHO) ( <sup>3</sup> A'')	113.06181	113.70306	113.99006	114.00106

<sup>a</sup> Frozen core approximation; see: De Frees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A. *J. Am. Chem. Soc.* 1982, 104, 5576. <sup>b</sup> The energy of the C(<sup>1</sup>D) is taken as the total energy of C(<sup>3</sup>P) and H<sub>2</sub>O plus the experimental separation of 30.0 kcal/mol. <sup>c</sup> Transition state from hydroxymethylene to formaldehyde.

and correlation is only 0.6 kcal/mol.

The geometry of triplet formaldehyde was taken from the Carnegie-Mellon Quantum Chemistry Archive at the 3-21G level.<sup>13</sup> The excitation energy S<sub>0</sub>-T<sub>1</sub> calculated at the UMP3/6-316G\*\* level agrees well with the experimental value<sup>21,26</sup> (calcd 73.3 kcal/mol; exptl 71.9 kcal/mol). The barrier from the triplet hydroxymethylene to triplet formaldehyde (nonplanar transition state, **7**) is calculated to be 41.3 kcal/mol (UMP3/6-31G\*\*),



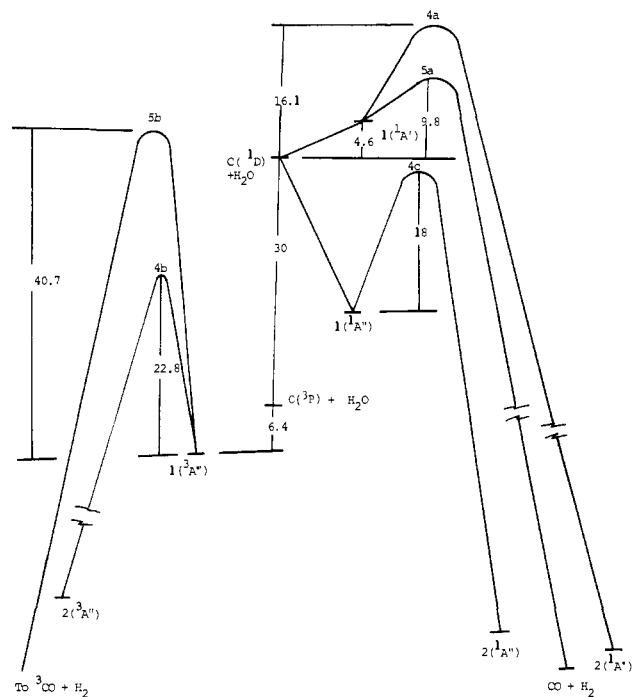
which is close to the singlet barrier of 38.9 kcal/mol. The barrier for the reverse reaction is much lower for the triplet (46.1 kcal/mol) compared to the closed-shell singlet (94.2 kcal/mol). It is, however, expected that intersystem crossing to the singlet hydroxymethylene might be more favorable than crossing the barrier to triplet formaldehyde.

A summary of total energies for the species indicated in Scheme I is given in Table VI.

(24) Pau, C.-F.; Hehre, W. J. *Phys. Chem.* 1982, 86, 1252.

(25) Frisch, M. J.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* 1981, 85, 1467.

(26) Herzberg, G. "Electronic Spectra of Polyatomic Molecules", Van Nostrand: New York, 1966.



**Figure 2.** Calculated energies of the reaction of  $C(^3P)$  and  $C(^1D)$  with  $H_2O$  and modes of decomposition of the initial  $C + H_2O$  complex.

### Experimental Results

The possible modes of reaction of carbon with water are summarized by the energy diagram in Figure 2.  $C(^1D)$  is predicted to react with  $H_2O$  along both closed- and open-shell energy surfaces. The closed-shell surface should generate  $CO + H_2$  via transition state **5a** with a barrier of 9.2 kcal/mol and hydroxymethylene (via **4a**) with a barrier of 16.1 kcal/mol. The lowest energy pathway on the open-shell surface for  $C(^1D)$  is rearrangement of the initial complex,  $1(^1A'')$ , to an excited singlet hydroxymethylene,  $2(^1A'')$ . Although the transition state, **4b**, for this process is 2.1 kcal/mol lower in energy than  $C(^1D) + H_2O$ , the  $\Delta H^\ddagger$  for the reaction from  $1(^1A'')$  is calculated to be 18.0 kcal/mol. Since  $C(^3P)$  is predicted to react with  $H_2O$  to generate complex  $1(^3A'')$  in which barriers to further reaction are higher than that for dissociation to carbon and water, triplet carbon atoms should be unreactive toward water.

These predictions of the relative reactivities of  $C(^3P)$  and  $C(^1D)$  toward  $H_2O$  are borne out by rate constants, which have been reported by Husain and Young,<sup>27</sup> for the reaction of carbon atoms, generated by the flash photolysis of  $C_3O_2$ , with water.  $C(^1D)$  is observed to react with  $H_2O$  approximately 17 times faster than  $C(^3P)$  does. Product studies were not reported in these flash photolysis investigations.

In order to carry out the experimental investigations of the reaction of carbon with water and identify the products, we have generated atomic carbon by the decomposition of 5-diazotetrazole, **8**.<sup>16</sup>

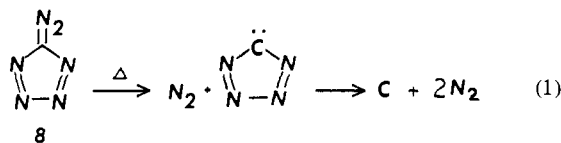


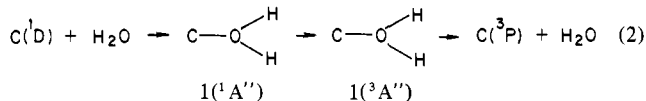
Table VII shows products and yields obtained when **8** is thermally decomposed in the presence of water vapor. Carbon monoxide and formaldehyde are the only products detected in appreciable amounts. Percent yields have been calculated by assuming that one carbon atom is generated for every three

**Table VII.** Products Formed in the Thermolysis of 5-Diazotetrazole (**8**) in the Presence of Water and/or  $O_2$

products <sup>a</sup>	reactants (mmol)		
	8 (1.94), $H_2O$ (1.03)	8 (1.94), $H_2O$ (1.01), $O_2$ (0.116)	8 (1.94), $O_2$ (0.116)
$N_2$	0.415	0.434	0.548
$CO$	$7.5 \times 10^{-3}$	$9 \times 10^{-2}$	$7.9 \times 10^{-2}$
$CH_2O$	$4.5 \times 10^{-3}$	$5 \times 10^{-3}$	
%CO	$9.5 \pm 3$	$53.7 \pm 8$	$47.5 \pm 9$
% $CH_2O$	$2.37 \pm 1$	$2.8 \pm 0.6$	

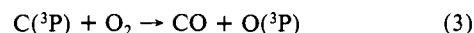
<sup>a</sup> Molar yields from typical runs appear in the rows corresponding to  $N_2$ ,  $CO$ , and  $CH_2O$ . Percent  $CO$  and  $CH_2O$  are calculated by assuming that one carbon atom is produced per three molecules of  $N_2$  and are the averages of four runs with appropriate standard deviations.

molecules of nitrogen produced. The observation of these two products is consistent with the calculations which predict two competing product-forming routes in the reaction of carbon atoms with water. The ratio of carbon monoxide to formaldehyde of approximately 4:1 indicates that the most favorable pathway is deoxygenation to generate  $CO + H_2$ . It is interesting that, although the transition state for deoxygenation is calculated to be at higher energy than that for rearrangement to  $2(^1A'')$ , deoxygenation is the major pathway. This predominance of deoxygenation over rearrangement may be explained by the fact that the lowest energy pathway for rearrangement to carbene  $2(^1A'')$  is via the open-shell complex  $1(^1A'')$ , which lies in a substantial energy well. Thus complex  $1(^1A'')$ , once formed, may not have sufficient energy to traverse the 18 kcal/mol barrier for rearrangement to  $2(^1A'')$ . An alternate reaction of  $1(^1A'')$  may be intersystem crossing to  $1(^3A'')$ , which could then dissociate to  $C(^3P) + H_2O$  (eq 2). Such a reaction would be reasonable as



the open-shell singlet  $1(^1A'')$  and triplet  $1(^3A'')$  complexes are calculated to have almost identical equilibrium geometries and the crossing rate should be rapid from the singlet to the triplet surface 19.7 kcal/mol lower in energy.

We may now turn our attention to an experimental evaluation of the spin state of the reacting carbon in this system. Flash photolysis studies have demonstrated that  $C(^3P)$  reacts with  $O_2$  at least an order of magnitude faster than with  $H_2O$  and that  $C(^1D)$  reacts with  $O_2$  and  $H_2O$  at comparable rates.<sup>27</sup> Although the product of the reaction of  $C(^1D)$  with  $O_2$  has not been determined, numerous chemical studies agree that the reaction of  $C(^3P)$  with  $O_2$  produces  $CO$  (eq 3).<sup>1b,c</sup> Thus, addition of  $O_2$  to



the  $C + H_2O$  system should allow a probe of the electronic state of the reacting carbon atom. If the reacting carbon is  $^3P$ , addition of a small amount of  $O_2$  to scavenge  $C(^3P)$  should reduce the formaldehyde yields. However, the data in Table VII indicate that the formaldehyde yields are unaffected by 11% added  $O_2$  while the  $CO$  yields increase dramatically. These results demonstrate that the precursor to formaldehyde cannot be  $C(^3P)$ , which would be scavenged by  $O_2$ , and must be  $C(^1D)$ .

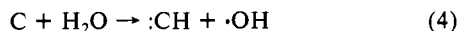
The fact that large amounts of  $C(^3P)$  are present but unreactive toward  $H_2O$  is indicated by the large increase in yields of  $CO$  when  $O_2$  is added. The yields of  $CO$  from the reaction of carbon with oxygen alone (Table VII) are invariably lower than those in the reaction between carbon, oxygen, and water. This result is consistent with the fact that there are two pathways to  $CO$  in the  $C + H_2O + O_2$  system but only one in the reaction between carbon and oxygen.

In general, atoms are expected to react with molecular substrates either by insertion or abstraction. In analogy with con-

(27) Husain, D.; Young, A. N. *J. Chem. Soc., Faraday Trans. 2* **1975**, 525.

(28) Hatakeyama, S.; Bandow, H.; Okuda, M.; Akimoto, H. *J. Phys. Chem.* **1981**, 85, 2249.

ventional radical chemistry, open-shell states are predicted to prefer abstraction while closed shells should insert. However, in the reaction between carbon and water, the abstraction route (eq 4)



is thermodynamically unfavorable for both C(<sup>1</sup>D) ( $\Delta H = 8.2$  kcal/mol) and C(<sup>3</sup>P) ( $\Delta H = 38.2$  kcal/mol). Thus the O-H bond strength appears to preclude abstraction along an open-shell energy surface. Abstractions by carbon are thought to lead to methylene, which, in the present case, is expected to react with water to generate methanol.<sup>28</sup> However, a careful search of the products of the C + H<sub>2</sub>O reaction does not reveal methanol.

### Conclusions

These investigations demonstrate the utility of combining a theoretical and experimental approach to the study of simple but highly reactive species such as carbon. The 3-21G basis is found to be adequate for geometry searches while the MP3/6-31G\*\* basis is flexible enough to give confidence to about 5 kcal/mol

after ZPC effects have been included.

In the reaction between carbon and water, singlet carbon atoms are predicted and observed to be reactive toward water by both insertion and deoxygenation. Triplet carbon atoms are predicted to be unreactive toward water. Oxygen-scavenging experiments confirm this prediction. The O-H bond strength precludes abstraction by both C(<sup>1</sup>D) and C(<sup>3</sup>P) and none is observed. We are currently investigating the reactions of other substrates with carbon from both a theoretical and experimental viewpoint in order to attempt to predict and explain reactivity patterns.

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**Registry No.** Carbon, 7440-44-0; water, 7732-18-5; hydroxymethylene, 19710-56-6.

## Microwave Structures of Cyanocyclopropane and Cyclopropylacetylene. Effects of Cyclopropyl $\pi$ Conjugation on Structure

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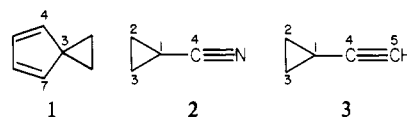
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**Abstract:** Microwave spectra of two isotopic forms of cyanocyclopropane and four isotopic forms of cyclopropylacetylene have been observed and analyzed. When these data were combined with previous measurements, complete heavy-atom substitution structures were determined. Among other parameters, the bond distances (Å) are as follows: for cyanocyclopropane, C<sub>1</sub>C<sub>2</sub> = 1.529 ± 0.005, C<sub>2</sub>C<sub>3</sub> = 1.500 ± 0.003, C<sub>1</sub>C<sub>4</sub> = 1.420 ± 0.006, C<sub>4</sub>N = 1.161 ± 0.004; for cyclopropylacetylene, C<sub>1</sub>C<sub>2</sub> = 1.527 ± 0.006, C<sub>2</sub>C<sub>3</sub> = 1.503 ± 0.007, C<sub>1</sub>C<sub>4</sub> = 1.422 ± 0.006, C<sub>4</sub>C<sub>5</sub> = 1.211 ± 0.004, C<sub>5</sub>H = 1.055 ± 0.003. The structural results have been compared to those in related molecules and are in accord with a simple theoretical model of  $\pi$ -electron donation from the cyclopropane ring to the  $\pi$  systems of the substituents. These data also point to the conclusion that cyclopropyl is a better donor than vinyl when these groups are conjugated with cyano or ethynyl.

### Introduction

Structural evidence for the  $\pi$ -conjugative interaction of the cyclopropyl ring has begun to emerge more clearly during the past few years. A recent contribution<sup>1,2</sup> from our laboratories has shown that the cyclopropyl group in spiro[2.4]hepta-4,6-diene (**1**) enters into effective  $\pi$  conjugation with the diene system. The experimental results are well described by a simple frontier orbital model<sup>1-3</sup> (Figure 1) which treats cyclopropyl as a  $\pi$ -electron donor. Allen<sup>4,5</sup> has recently surveyed a large amount of X-ray diffraction data and his analysis provides strong evidence for the universality of this behavior for various cyclopropyl systems with  $\pi$ -acceptor substituents. The subject has also been addressed theoretically by means of ab initio calculations.<sup>2,6-8</sup>

In the present study we report the complete heavy-atom structures of two of the simplest molecules for which this cyclopropyl  $\pi$  conjugation is possible, viz., cyanocyclopropane (**2**) and cyclopropylacetylene (**3**). An earlier microwave structural study<sup>9</sup> of **2** provided ring data but no structural parameters for the cyano (nitrile) group, whereas an NMR study of partially oriented **2** provided the relative proton structure.<sup>10</sup> A microwave study of **3** yielded no reliable structural data,<sup>11</sup> and an electron diffraction study that appeared after the present work was underway provided only partly reliable results.<sup>12</sup>



**Spectral Samples.** Commercially available cyanocyclopropane (Aldrich) was used for spectral surveys of the normal isotopic species and also for some observations of the 1-<sup>13</sup>C and 2-<sup>13</sup>C

- (1) Staley, S. W.; Howard, A. E.; Harmony, M. D.; Mathur, S. N.; Kattija-Ari, M.; Choe, J.-I.; Lind, G. *J. Am. Chem. Soc.* **1980**, *102*, 3639.
- (2) Harmony, M. D.; Mathur, S. N.; Choe, J.-I.; Kattija-Ari, M.; Howard, A. E.; Staley, S. W. *J. Am. Chem. Soc.* **1981**, *103*, 2961.
- (3) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907.
- (4) Allen, F. H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 81.
- (5) Allen, F. H. *Acta Crystallogr., Sect. B* **1981**, *B37*, 890.
- (6) Skancke, A.; Boggs, J. E. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 893.
- (7) Skancke, A.; Boggs, J. E. *J. Mol. Struct.* **1979**, *51*, 267.
- (8) Oberhammer, H.; Boggs, J. E. *J. Mol. Struct.* **1979**, *57*, 175.
- (9) Pearson, R., Jr.; Choplin, A.; Laurie, V. W. *J. Chem. Phys.* **1975**, *62*, 4859.
- (10) Cole, K. C.; Gilson, D. F. R. *Can. J. Chem.* **1976**, *54*, 2788.
- (11) Collins, M. J.; Britt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1972**, *56*, 4262.
- (12) Klein, A. W.; Schrupf, G. *Acta Chem. Scand. A* **1981**, *35*, 431.
- (13) Allen, C. F. H. "Organic Syntheses", 2nd ed.; Wiley: New York, 1941; Coll. Vol. I, p 156.

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