J. Am. Chem. Soc. 1993, 115, 6904–6907

The Attractive Quartet Potential Energy Surface for the CH(a $^4\Sigma^-$) + CO Reaction: A Role for the a $^4A''$ State of the Ketenyl Radical in Combustion?

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Received March 18, 1993

Abstract: *Ab initio* quantum mechanical techniques, including the self-consistent-field (SCF), single and double excitation configuration interaction (CISD), single and double excitation coupled cluster (CCSD), and the single, double, and perturbative triple excitation coupled cluster [CCSD(T)] methods have been applied for the study of the HCCO(a $^4A''$) energy hypersurface. Rate constant measurements suggest an attractive potential for the reaction of CH(a $^4\Sigma^-$) with CO. A vanishingly small energy barrier is predicted here in the CH(a $^4\Sigma^-$) + CO reaction channel. We propose that a spin-forbidden electronic deactivation of CH(a $^4\Sigma^-$) might occur through an intersystem crossing involving the a $^4A''$ state of HCCO. The energetics and the geometries of the reactants and products on both quartet and doublet energy surfaces are presented. The relationship between this research and experimental combustion chemistry is explored.

Introduction

Fenimore and Jones[1] first suggested that the reaction of oxygen atoms with acetylene might form the ketenyl radical, HCCO, in addition to other products:

$$O(^3P) + C_2H_2 \rightarrow HCCO + H \qquad (1a)$$

$$\rightarrow CH_2 + CO \qquad (1b)$$

There has been considerable controversy about whether channel 1a or 1b is more important; recent work[2] concludes that for the homogeneous thermal reaction, channel 1a accounts for about 70% of this reaction. Since acetylene is formed as an intermediate in most hydrocarbon combustion processes[3] and since the dominant loss of C_2H_2 is by reaction with oxygen atoms,[4] HCCO must be a common radical in hydrocarbon flames.

Although important, the ketenyl radical HCCO is difficult to detect and so has received less attention than other combustion related radicals. HCCO was first observed in the gas phase by mass spectrometry.[5] Only recently has it been possible to identify HCCO by microwave spectrometry[6] and by infrared absorption.[7] No electronic spectrum of HCCO is yet known.[8] Two *ab initio* predictions[9] on the structure of ground state HCCO appear to be in reasonable agreement with the limited structural data.[5]

The metastable quartet state of methyne, CH(a $^4\Sigma^-$), is another combustion intermediate that has been neglected because it is difficult to detect. CH(a $^4\Sigma^-$) was predicted in 1973 by Lie, Hinze, and Liu[10] to lie 0.62–0.76 eV above the ground CH(X $^2\Pi$) state. Electron photodetachment experiments on CH^- by Kasdan, Herbst, and Lineberger[11] lead to the conclusion that the energy difference between these two states is 0.74 eV, agreeing well with the theoretical result of Liu *et al.*[10] The most recent theoretical result for this difference falls in the range 0.56–0.70 eV.[12] CH(a $^4\Sigma^-$) has been identified by laser magnetic resonance in the reaction of oxygen atoms with acetylene,[13] and its concentration can be monitored by chemi-ionization.[14] Some rate constants for reactions of CH(a $^4\Sigma^-$) are now becoming available.[15]

The kinetic behavior of CH(a $^4\Sigma^-$) is different from that of the ground state, CH(X $^2\Pi$). Metastable CH(a $^4\Sigma^-$) is quite unreactive toward most closed-shell molecules.[15] One exception is reaction 2, which has a slow but measurable rate.

$$CH(a\,^4\Sigma^-) + CO(X\,^1\Sigma^+) \rightarrow \text{products} \qquad (2)$$

Since there is no spin-allowed channel for this exoergic reaction, it was suggested[15c] that there might be an attractive quartet surface leading to a metastable quartet state of HCCO. This could allow sufficient interaction time for an intersystem crossing to occur, resulting in electronic deactivation of the CH(a $^4\Sigma^-$) state. The present theoretical study was initiated in order to explore the possibility of a quartet state of HCCO playing a significantl role in this chemistry.

Theoretical Approach and Results

Geometries of HCCO, CH, and CO were optimized with the self-consistent-field (SCF)[16] and the single and double excitations

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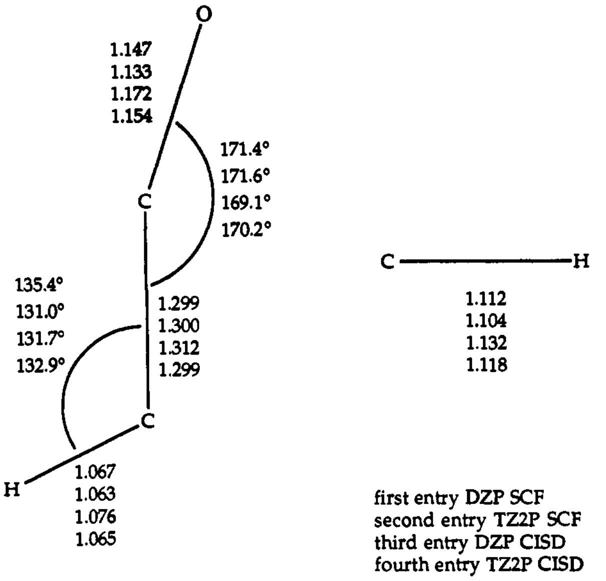

first entry DZP SCF
second entry TZ2P SCF
third entry DZP CISD
fourth entry TZ2P CISD

Figure 1. Geometrical parameters for ground state CH(X $^2\Pi$) and HCCO(X $^2A''$). Bond distances are in angströms.

configuration interaction (CISD)[17] analytic gradient methods. Assuming the stationary point geometries obtained at the CISD level of theory, we have also applied the single and double excitations coupled cluster (CCSD) method and the newer method designated CCSD(T) by Raghavachari, Trucks, Pople, and Head-Gordon,[18] which includes all triple excitations in a noniterative manner. The CCSD(T) method[19] is one of the most powerful practical electronic structure methods for open-shell molecules, and it has been recently applied to the related triplet HCCN molecule by Seidl and Schaefer.[20]

Basis sets used in this study are the double-ζ plus polarization (DZP, Huzinaga-Dunning[21,22]) and triple-ζ plus double polarizations (TZ2P, Huzinaga-Dunning[21,23]). The DZP basis set is designated as C, O(9s5p1d/4s2p1d), H(4s1p/2s1p). Orbital exponents for the polarization functions are $\alpha_d(\mathrm{C}) = 0.75$, $\alpha_d(\mathrm{O}) = 0.85$, and $\alpha_p(\mathrm{H}) = 0.75$. The TZ2P basis set is designated as C, O(10s6p2d/5s3p2d), H(5s2p/3s2p), with polarization function orbital exponents $\alpha_d(\mathrm{C}) = 1.5, 0.375$, $\alpha_d(\mathrm{O}) = 1.7, 0.425$, and $\alpha_p(\mathrm{H}) = 1.5, 0.375$. Pure sets of d functions (i.e., five d functions) were used in this study.

With the CISD, CCSD, and CCSD(T) methods, the three lowest occupied molecular orbitals (C, O 1s like orbitals) were held doubly occupied and the three highest lying virtual orbitals (antibonding core counterparts) were deleted in all configurations. At the CISD level of theory, the total energy of (free) CH plus CO was obtained by separating the two species at 500 au (supermolecule) to overcome the failure of the CI method to be size-consistent. Computations were carried out with the PSI suite of programs.[24]

The geometrical parameters and energetics of the ground state HCCO(X $^2A''$) are summarized in Figure 1 and Table I, respectively. Geometrical parameters obtained at the TZ2P CISD level of theory are summarized in Table II, and the theoretical predicted geometrical parameters agree well with previous theoretical[9a,b] and experimental values. The short C–C bond suggests double bond character, and thus the electronic structure is best described as H—$\dot{\mathrm{C}}$=C=O. No cis HCCO doublet structure was located. The doublet energy surface is attractive, and the dissociation energy (D_e) is 67 kcal/mol at the TZ2P CCSD(T) level of theory, taking this energy difference to be ΔE for

Table I. Theoretical Total Energies (au) for HCCO(X $^2A''$), CH(X $^2\Pi$), and CO(X $^1\Sigma^+$) and the Dissociation Energy (D_e, kcal/mol) of Doublet HCCO[a]

	HCCO	CH	CO	D_e
DZP SCF	−151.103 979	−38.271 821	−112.758 921	46.0
TZ2P SCF	−151.132 995	−38.277 089	−112.781 618	46.6
DZP CISD	−151.478 842	−151.380 890[b]		61.5
TZ2P CISD	−151.557 643	−151.457 490[b]		62.9
DZP CCSD	−151.522 127	−38.378 905	−113.043 222	62.8
TZ2P CCSD	−151.606 839	−38.397 492	−113.108 158	63.5
DZP CCSD(T)	−151.539 49	−38.380 767	−113.053 323	66.1
TZ2P CCSD(T)	−151.630 659	−38.400 359	−113.123 132	67.3

[a] Energy difference for HCCO($^2A''$) → CH($^2\Pi$) + CO($^1\Sigma^+$). [b] Supermolecule results, CH and CO separated by 500 au.

Table II. Comparison of the Present Theoretical Bond Distances and Angles with Those Predicted by Others and with Experimental Values[a]

	theoretical predictions			experiment	
	Harding[9a]	Goddard[9b]	this work	parameter	ref
HCCO(X $^2A''$)					
CH, Å	[1.09]	1.074	1.065	1.056	6
CC, Å	1.326	1.301	1.299	1.314	6
CO, Å	1.153	1.170	1.154	[1.150]	6
<CCH, deg	132	133	133	139	6
<CCO, deg	166	170	170	[180]	6
CO(X $^1\Sigma^+$), Å			1.122	1.1283	27
CH(X $^2\Pi$), Å			1.118	1.1199	27
CH(a $^4\Pi^-$), Å			1.086	1.0977	13

$$\mathrm{HCCO(X\ ^2A'')} \rightarrow \mathrm{CH(X\ ^2\Pi^-)} + \mathrm{CO(X\ ^1\Sigma^+)} \quad (3)$$

For the quartet HCCO radical we have examined three structures, the cis and trans conformations and the transition state for dissociation, as shown in Figure 2. The theoretical predicted geometrical parameters (Figure 2) are similar for the cis and trans structures of HCCO. However, the geometry of the quartet state of HCCO is quite different from that of the doublet HCCO; the C-C-O bond angle is much more bent (~120°), and the three quartet bond distances are all longer than those of doublet HCCO. The bond distances and bond angles suggest that the HCCO quartet state basically consists of a carbene-like counterpart and a carbonyl radical, which can be qualitatively described as H—$\ddot{\mathrm{C}}$—$\dot{\mathrm{C}}$=O. The C-H and C-O bond lengths of the transition state are close to those of free CH and CO, with the long (dissociating HCCO → HC + CO) C-C bond length being about 2.1 Å.

According to our vibrational frequency analyses with the DZP and TZ2P SCF methods, both cis and trans structures are minima (no imaginary vibrational frequency) on the energy hypersurface. For the dissociation transition state imaginary frequencies of 752 and 745 cm⁻¹ were obtained from the DZP SCF and TZ2P SCF methods, respectively.

The cis form of quartet HCCO is lower in energy than the trans form at all levels of theory (see Table III). The dissociation energy (D_e) was thus evaluated from the energy difference of

$$\mathrm{HCCO(a\ ^4A'',cis)} \rightarrow \mathrm{CH(a\ ^4\Sigma^-)} + \mathrm{CO(X\ ^1\Sigma^+)} \quad (4)$$

The D_e obtained from this equation is summarized in Table III, where we see that the energy surface of the quartet CH + CO

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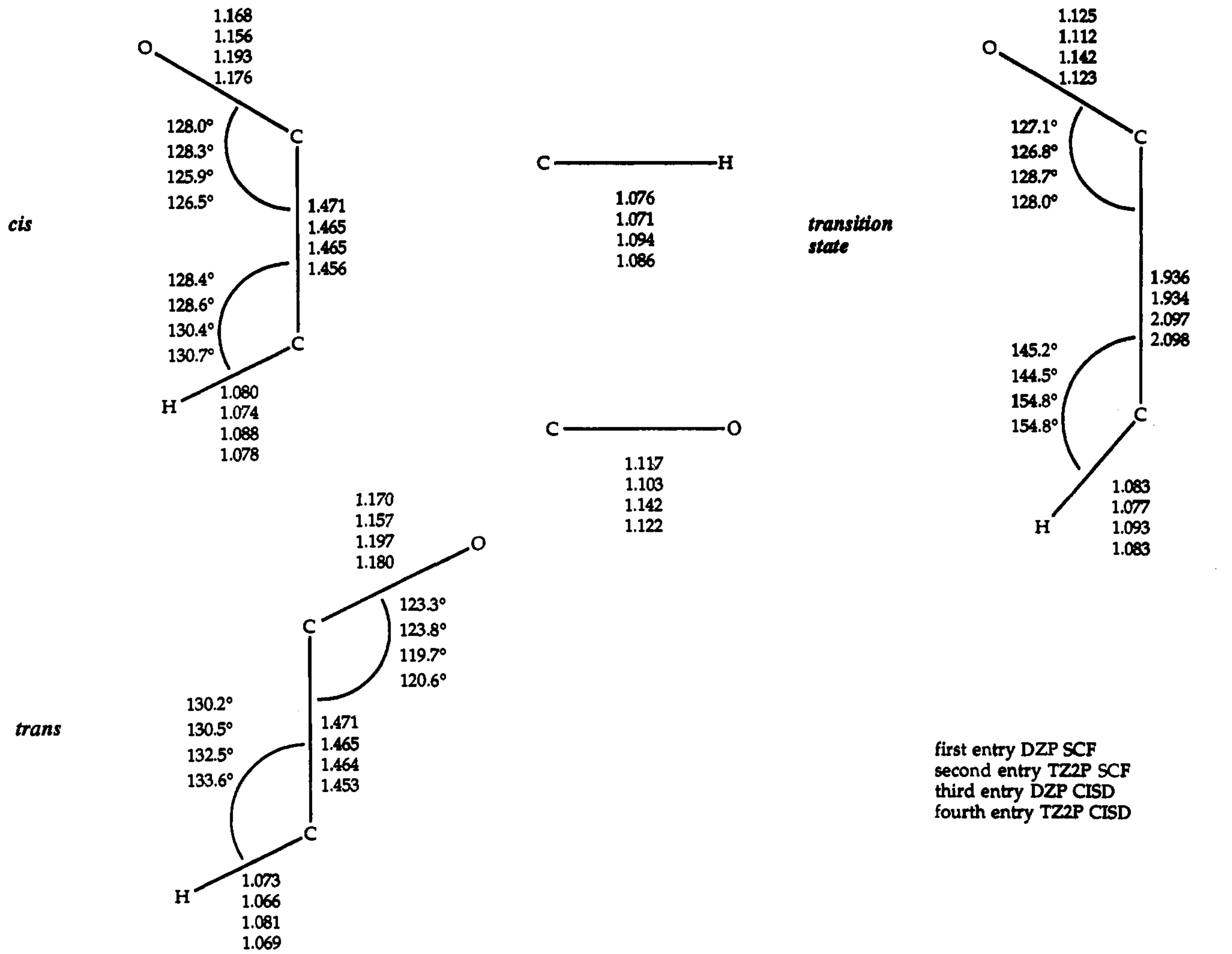

Figure 2. Theoretical geometrical parameters for CH(a $^4\Sigma^-$), CO, *cis* and *trans* quartet HCCO and the transition state for the dissociation of HCCO(a $^4A''$). Bond distances are in angströms.

Table III. Theoretical Total Energies (au) for HCCO(a $^4A''$; Cis, Trans, and the Transition State for Dissociation), CH(a $^4\Sigma^-$), and CO($^1\Sigma^+$), Dissociation Energy (D_e kcal/mol) for the Cis Isomers of Quartet HCCO, and Activation Energy (E_a, kcal/mol) for CH + CO[a]

	cis	trans	transition state	CH	CO	E_a	D_e
DZP SCF	−151.058 987	−151.044 991	−151.019 195	−38.283 947	−112.758 921	14.9	10.1
TZ2P SCF	−151.082 787	−151.068 857	−151.044 702	−38.288 014	−112.781 618	15.6	8.3
DZP CISD	−151.408 261	−151.395 651	−151.362 567	−151.370 378[b]		4.9	23.8
TZ2P CISD	−151.480 883	−151.468 485	−151.437 075	−151.444 968[b]		5.0	22.5
DZP CCSD	−151.445 912	−151.433 929	−151.400 699	−38.360 048	−113.043 222	1.7	26.7
TZ2P CCSD	−151.524 672	−151.512 999	−151.481 744	−38.375 166	−113.108 158	1.4	25.6
DZP CCSD(T)	−151.459 039	−151.447 210	−151.413 694	−38.361 242	−113.053 323	0.6	27.9
TZ2P CCSD(T)	−151.544 239	−151.532 777	−151.500 738	−38.377 559	−113.123 132	0.0	27.3

[a] Energy difference for HCCO($^4A''$; cis) → CH($^4\Sigma^-$) + CO($^1\Sigma^+$). [b] Supermolecule results, CH and CO separated by 500 au.

is attractive, by about 27 kcal/mol from our TZ2P CCSD(T) result. Normally one would expect this prediction to be smaller than the true dissociation energy, but the theoretical difficulty of describing the triple bond in isolated carbon monoxide may neutralize the traditional thinking in this regard.

In the evaluation of the association [CH(a $^4\Sigma^-$) + CO(X $^1\Sigma^+$) → HCCO(a $^4A''$)] barrier E_a, we found that the barrier decreases as the higher levels of correlated methods CCSD and CCSD(T) are applied. The barrier is ~5 kcal/mol at the CISD level of theory with both DZP and TZ2P basis sets. However, at the TZ2P CCSD(T) level the barrier appears to vanish. Since these energies were computed at the geometries obtained at the CISD method with the same basis sets, we do not definitely predict a vanishing barrier. Therefore it is possible that a very small barrier exists, probably less than 2 kcal/mol. The more accurate characterization would require locating the geometries of the transition state and the separated species (CH and CO) with the coupled cluster method. Qualitative energetics of the quartet and doublet species (including the transition state) are shown in Figure 3.

Conclusions

We have located two minima for the quartet HCCO(a $^4A''$) radical—the cis and trans structures, and the transition state in the quartet CH + CO reaction channel. The cis quartet structure is lower in energy than the trans structure at all levels employed in our theoretical approach. The geometry of HCCO(a $^4A''$) suggests that this molecule involves essentially a carbene-like counterpart and a carbonyl carbon radical. We have also presented theoretical geometries for HCCO(X $^2A''$) and the energetics of the species involved in both the quartet and doublet

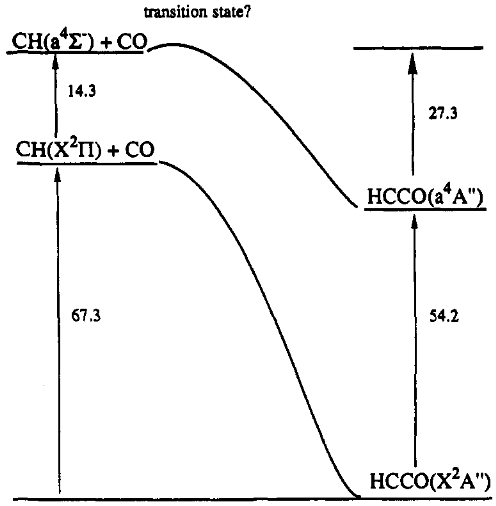

Figure 3. Energetics on the quartet and doublet HCCO potential energy surfaces. Indicated energy differences are TZ2P CCSD(T) results.

CH + CO reactions. Our best theoretical result [TZ2P CCSD(T)] predicts 27 kcal/mol for the energy difference between CH(a $^4\Sigma^-$) + CO(X $^1\Sigma^+$) and HCCO(a $^4A''$).

The observation of potential minima on the quartet HCCO hypersurface supports the proposal that the observed destruction of CH(a $^4\Sigma^-$) by CO is an electronic deactivation. Two molecules approaching along the quartet surface would encounter a barrier of at most 2 kcal/mol, followed by a potential well approximately 29 kcal/mol deep. With six vibrational degrees of freedom, the hot HCCO(a $^4A''$) should be trapped in this well for many vibrations. Being a carbonyl compound, intersystem crossing (a $^4A'' \rightarrow X\,^2A''$) would be likely, resulting in a ground state HCCO with approximately 80 kcal/mol of vibrational energy. This very hot HCCO(X $^2A''$) should dissociate rapidly to ground state CH(X $^2\Pi$) + CO. Other examples of spin-forbidden deactivations in a potential well include O(^{1}D) + N_2 and O(^{1}D) + CO_2,[25] in addition to singlet CCO + CO.[26]

If the above interpretation is correct, the rate constant for reaction 2 should be independent of pressure, as is observed,[15c] and should increase with increasing temperature. The experimental value for k_2 of 8×10^{-13} cm³ molecule⁻¹ s⁻¹ at 297 K and the calculated activation energy suggest the Arrhenius expression

$$k_2 = (2.3 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}})\ \exp(-1000/T)$$

The resulting preexponential factor is quite reasonable, being close to the collision frequency. Further experiments will be needed to test this expression.

Since HCCO is a common radical in flames, it is likely that some of it will be in the metastable quartet state. While reaction 1a is not sufficiently exoergic to form a $^4A''$ HCCO directly, it is likely that some quartet states would form by energy transfer, for example,

$$\mathrm{HCCO(X\,^2A'') + CO(a\,^3\Pi) \rightarrow HCCO(a\,^4A'') + CO(X\,^1\Sigma^+)} \quad (5)$$

A vibrationally relaxed HCCO(a $^4A''$) should have a long radiative lifetime since the electronic transition will be spin-forbidden and there are significant differences in the geometries of the ground and metastable states (in particular, the CC bond distances and the CCO angles). Consequently reactions of HCCO(a $^4A''$) may be significant in flames.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant No. DE-FG09-87ER13811.

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