Characterization of the minimum energy paths for the ring closure reactions of C_4H_3 with acetylene

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The ring closure reaction of C_4H_3 with acetylene to give phenyl radical is one proposed mechanism for the formation of the first aromatic ring in hydrocarbon combustion. There are two low-lying isomers of C_4H_3; 1-dehydro-buta-1-ene-3-yne (n-C_4H_3) and 2-dehydro-buta-1-ene-3-yne (iso-C_4H_3). It has been proposed that only n-C_4H_3 reacts with acetylene to give phenyl radical, and since iso-C_4H_3 is more stable than n-C_4H_3, formation of phenyl radical by this mechanism is unlikely. We report restricted Hartree–Fock (RHF) plus singles and doubles configuration interaction calculations with a Davidson's correction (RHF+1+2+Q) using the Dunning correlation consistent polarized valence double zeta basis set (cc-pVDZ) for stationary point structures along the reaction pathway for the reactions of n-C_4H_3 and iso-C_4H_3 with acetylene. n-C_4H_3 plus acetylene (9.4) has a small entrance channel barrier (17.7) (all energetics in parentheses are in kcal/mol with respect to iso-C_4H_3 plus acetylene) and the subsequent closure steps leading to phenyl radical (−91.9) are downhill with respect to the entrance channel barrier. Iso-C_4H_3 plus acetylene also has an entrance channel barrier (14.9) and there is a downhill pathway to 1-dehydro-fulvene (−55.0). 1-dehydro-fulvene can rearrange to 6-dehydro-fulvene (−60.3) by a 1,3-hydrogen shift over a barrier (4.0), which is still below the entrance channel barrier, from which rearrangement to phenyl radical can occur by a downhill pathway. Thus, both n-C_4H_3 and iso-C_4H_3 can react with acetylene to give phenyl radical with small barriers. © *1995 American Institute of Physics.*

I. INTRODUCTION

The formation of the first aromatic ring (phenyl radical) is widely believed to be the rate limiting step in the formation of soot in hydrocarbon combustion. One mechanism for the formation of phenyl radical involves the stepwise addition of acetylenes.[1] One possible pathway is the reaction of the vinyl radical with acetylene to give C_4H_3 followed by subsequent addition of another acetylene and ring closure to give phenyl radical. Another pathway to C_4H_3 is the reaction of vinylidene with acetylene to give vinylacetylene (buta-1-ene-3-yne),[2] which can be converted to C_4H_3 (1- or 2-dehydro-buta-1-ene-3-yne) by abstraction of a hydrogen. Note that reaction of acetylene with itself does not occur by any low energy pathway, and vinylidene is 43 kcal/mol above acetylene;[2,3] thus, the formation of vinylacetylene from two acetylenes requires a moderate activation energy. The structure and properties of C_4H_3 have been studied by Ha and Gey[4] using PUMP4/6-31G** theory. They find two low-lying isomers 1-dehydro-buta-1-ene-3-yne (n-C_4H_3) and 2-dehydro-buta-1-ene-3-yne (iso-C_4H_3). Iso-C_4H_3 is found to be 7.3 kcal/mol below n-C_4H_3 (including zero-point effects). Miller and Melius[5] also noted that iso-C_4H_3 is thermodynamically more stable than n-C_4H_3 and thus most of the C_4H_3 should be in the form of the iso isomer even at combustion temperatures. Thus, it is of interest to study the reaction of both iso-C_4H_3 and n-C_4H_3 with acetylene, as discussed herein.

In Sec. II the technical details of the calculations are discussed, while Sec. III discusses the results, and Sec. IV concludes the paper.

II. COMPUTATIONAL DETAILS

Two different basis sets were used in these calculations. The stationary points were located with restricted Hartree–Fock (RHF) derivative calculations using the valence double zeta set of Dunning and Hay.[6] The basis set for C is the $(9s5p)/[3s2p]$ basis and the H basis is $(4s)/[2s]$, i.e., the polarization functions are omitted. The subsequent internally contracted configuration interaction (ICCI) calculations were based on the RHF reference wave function and used the Dunning correlation consistent polarized valence double zeta basis set.[7]

The geometry optimizations used the SIRIUS/ABACUS system of programs,[8] while the ICCI calculations were carried out with MOLPRO.[9,10] All electrons were correlated except for the C 1s like electrons. A multireference analog of the Davidson's correction[11] was added to the ICCI energies and is denoted by $+Q$.

III. DISCUSSION

Table I(a) shows the computed ICCI energies of the stationary point structures for the reaction of iso-C_4H_3 with acetylene, while Table I(b) shows the same information for the reaction of n-C_4H_3 with acetylene. The computed harmonic frequencies are given in Tables AIa and AIb of the PAPS material.[12] The zero point effects were estimated as 1/2 the sum of the harmonic frequencies and these are included in the relative energies, which are given in the last column of Tables I(a) and I(b). Finally, the Cartesian coordinates for the stationary points are given in Tables AIIa and AIIb of the PAPS material.

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TABLE I. (a) Computed energies for stationary points on the iso-C_4H_3 plus C_2H_2 surface.[a] (b) Computed energies for stationary points on the n-C_4H_3 plus C_2H_2 surface.[b]

Geometry	ICCI (ICCI+Q+230.)	ZPE	ΔE
	(a)		
reac	−230.551 40(−0.685 46)	0.075 38	0.0
sp1	−230.530 32(−0.668 48)	0.082 08	14.9
min1	−230.612 79(−0.742 74)	0.087 99	−28.0
sp3	−230.602 14(−0.733 03)	0.085 70	−23.4
min3	−230.612 50(−0.742 39)	0.087 84	−27.9
sp6	−230.586 35(−0.719 08)	0.086 60	−14.1
min6	−230.657 85(−0.789 94)	0.092 23	−55.0
sp7	−230.553 15(−0.688 29)	0.084 52	4.0
min7	−230.665 83(−0.797 63)	0.091 41	−60.3
sp8	−230.601 10(−0.734 03)	0.086 29	−23.6
min8	−230.610 98(−0.741 16)	0.087 99	−27.0
sp9	−230.529 84(−0.664 82)	0.082 95	17.7
min9	−230.659 85(−0.791 56)	0.091 76	−56.3
sp10	−230.587 26(−0.720 29)	0.086 40	−14.9
min10	−230.618 72(−0.748 86)	0.086 78	−32.6
	(b)		
reactants	−230.537 98(−0.671 01)	0.075 87	9.4
sp2	−230.530 09(−0.663 57)	0.081 72	17.7
min2	−230.605 13(−0.737 60)	0.088 29	−24.6
sp4	−230.595 01(−0.728 48)	0.085 96	−20.4
min4	−230.610 98(−0.741 16)	0.087 99	−27.0
sp5	−230.589 19(−0.729 47)	0.087 62	−19.9
min5	−230.720 30(−0.850 62)	0.094 09	−91.9

[a]Energies in a.u. except for ΔE which is the relative energy in kcal/mol with respect to iso-C_4H_3+C_2H_2 including zero point energy.
[b]Energiees in a.u. except for ΔE which is the relative energy in kcal/mol with respect to iso-C_4H_3+C_2H_2 including zero point energy.

The stationary points structures for the reaction of iso-C_4H_3 with acetylene are shown in Fig. 1, while those for the reaction of n-C_4H_3 with acetylene are shown in Fig. 2. Figure 3 shows the stationary point structures for the conversion of min6 to min10. (Here structures denoted by min are minima and structures denoted by sp are saddle points on the potential energy surface.) The energetics for these processes are shown in Figs. 4–6, respectively.

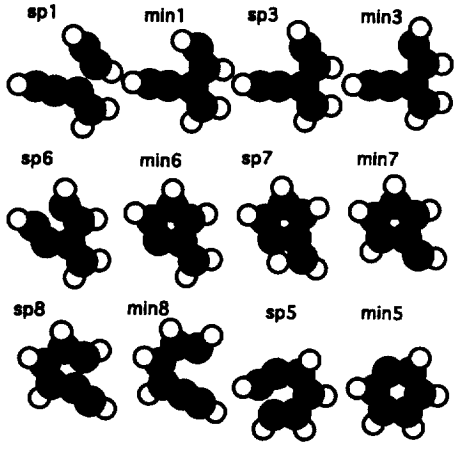

FIG. 1. Stationary point structures for the reaction of iso-C_4H_3+C_2H_2→C_6H_5 (phenyl). The following nomenclature is used. Min1 and min3=1-dehydro-3-methylene-penta-1-ene-4-yne. Min6=1-dehydro-fulvene. Min7=6-dehydro-fulvene. Min8=1-dehydro-hexa-1,3-diene-5-yne =Min4. Min5-phenyl radical. Structures designated by min are minima on the PES while structures designated by sp are saddle points. This convention is also used for Figs. 2 and 3.

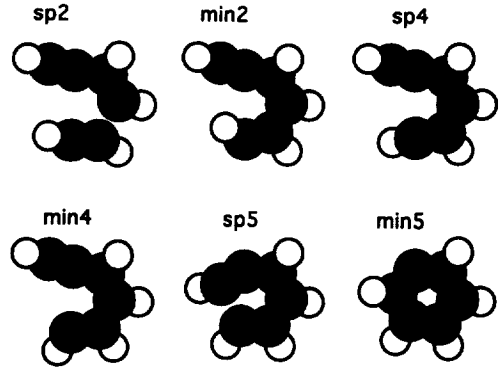

FIG. 2. Stationary point structures for the reaction of n-C_4H_3+C_2H_2→C_6H_5 (phenyl). The following nomenclature is used. Min2 and min4=1-dehydro-hexa-1,3-diene-5-yne. Min5=phenyl radical.

Consider first the entrance channel barriers for the reaction of n-C_4H_3 and iso-C_4H_3 with acetylene. n-C_4H_3 plus acetylene is 9.4 kcal/mol above iso-C_4H_3 plus acetylene, but the barrier to addition is 14.9 kcal/mol for iso-C_4H_3 plus acetylene and 8.3 kcal/mol for n-C_4H_3 plus acetylene. The higher barrier for iso-C_4H_3 plus acetylene probably results from larger nonbonding interactions between the two acetylenic groups, which come closer together in the iso-C_4H_3 plus acetylene case. This is reflected in the larger angle between the acetylenic groups in Fig. 1 as compared to Fig. 2.

Addition of n-C_4H_3 to acetylene leads to min2. Inversion about the CH group of C1 interconverts min2 and min4 with a barrier of 4.2 kcal/mol. Min4 closes to min5 (phenyl radical) with only a small barrier. Thus, this reaction path leads to phenyl radical with no barrier other than the entrance channel addition barrier.

Addition of iso-C_4H_3 to acetylene leads to min1. Min1 is connected to min3 by sp3. The conversion from min1 to

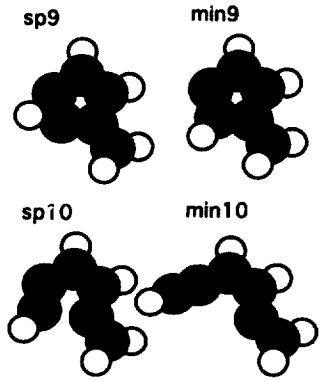

FIG. 3. Stationary point structures for the conversion of min6 to min10. The following nomenclature is used. Min9=2-dehydro-fulvene. Min10=2-dehydro-hexa-1,3-diene-5-yne.

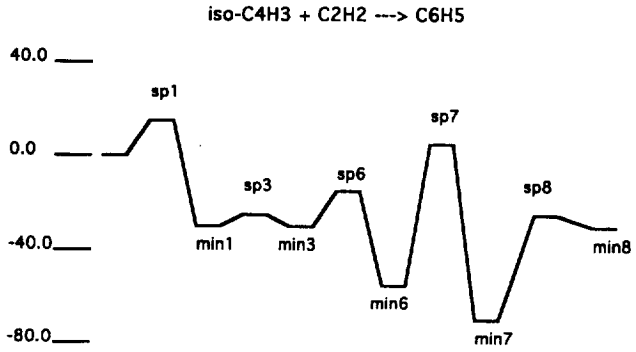

FIG. 4. Energetics from SDCI+Q calculations with the cc-pVDZ basis set for iso-C_4H_3+C_2H_2→C_6H_5 (phenyl).

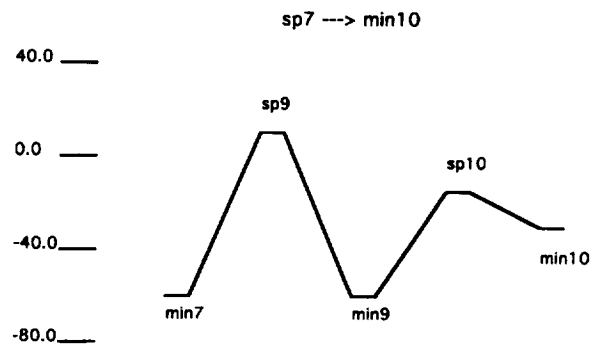

FIG. 6. Energetics from SDCI+Q calculations with the cc-pVDZ basis set for the conversion of min6 to min10.

min3 involves an inversion of the CH group about C1. This involves only a 4.6 kcal/mol barrier. Sp6 connects min3 to min6 (1-dehydro-fulvene). Sp7 is the saddle point for a 1,3-hydrogen shift which connects min6 (1-dehydro-fulvene) to min7 (5-dehydro-fulvene). This process involves a large barrier; sp7 is 4 kcal/mol above iso-C_4H_3 plus acetylene, but still below the entrance channel saddle point, so this channel is energetically accessible. Min7 can convert to min8 via sp8. Min8 is the same structure as min4 in the n-C_4H_3 plus acetylene reaction pathway. This can then convert to phenyl radical via a downhill pathway. Thus, both iso-C_4H_3 plus acetylene and n-C_4H_3plus acetylene can give phenyl radical by pathways which involve no barriers, which are larger than the entrance channel addition barriers.

Sp9 is a saddle point connecting min7 to min9 (2-dehydro-fulvene). Sp9 is 17.7 kcal/mol above iso-C_4H_3 plus acetylene, which is still below the entrance channel saddle point. However, sp9 is a second order saddle point, i.e., it has two negative eigenvalues [see Table I(a)] one of which leads to symmetry breaking. Thus, there may be a lower energy path to min9 if the symmetry is lowered. This point was not examined further in this work. Sp10 connects min9 to min10.

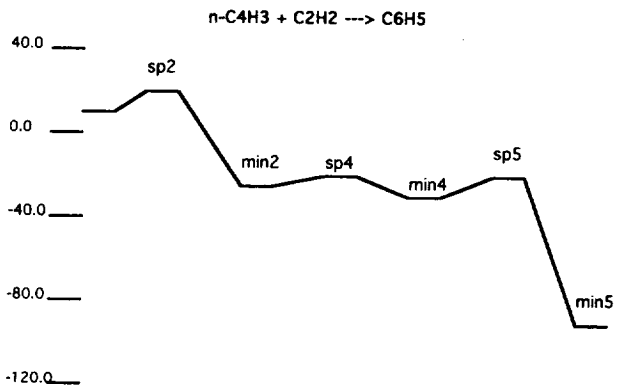

FIG. 5. Energetics from SDCI+Q calculations with the cc-pVDZ basis set for n-C_4H_3+C_2H_2→C_6H_5 (phenyl).

IV. CONCLUSIONS

The ring closure reactions of 1-dehydro-buta-1-ene-3-yne (n-C_4H_3) and 2-dehydro-buta-1-ene-3-yne (iso-C_4H_3) with acetylene have been studied using RHF plus singles and doubles CI plus a Davidson's correction with the Dunning cc-pVDZ basis set at stationary point structures determined by RHF derivative calculations using a polarized valence double zeta basis set. Zero-point effects were estimated based on the RHF harmonic frequencies.

n-C_4H_3 plus acetylene (9.4) has a small entrance channel barrier (17.7) (all energetics in parentheses are in kcal/mol with respect to iso-C_4H_3 plus acetylene) and the subsequent closure steps leading to phenyl radical (−91.9) are downhill with respect to the entrance channel barrier. Iso-C_4H_3 plus acetylene also has an entrance channel barrier (14.9) and there is a downhill pathway to 1-dehydro-fulvene (−55.0). 1-dehydro-fulvene can rearrange 6-dehydrofulvene (−60.3) by a 1,3-hydrogen shift over a barrier (4.0), which is still below the entrance channel barrier. 6-dehydro-fulvene can rearrange to phenyl radical via 1-dehydro-hexa-1,3-diene-5-yne (−27.0). Thus, both n-C_4H_3 and iso-C_4H_3 can react with acetylene to give phenyl radical with small barriers.

With respect to iso-C_4H_3 plus acetylene, all of the open structures (min1, min3, min8=min4, and min10) are from 27.0 to 32.6 kcal/mol lower, while the dehydro-fulvene structures (min6, min7, and min9) are from 55.0 to 60.3 kcal/mol lower, and the phenyl radical is 91.9 kcal/mol lower, respectively. Thus, since all these structures can interconvert with barriers below the entrance channel barrier, the ultimate product is expected to be phenyl radical, although other C_6H_5 species may still play a role as reactive intermediates.

ACKNOWLEDGMENTS

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