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A crossed molecular beams study on the formation and energetics of the resonantly stabilized free *i*-$C_4H_3(X^2A')$ radical and its isotopomers

Xibin Gu [a], Ying Guo [a], Fangtong Zhang [a], Alexander M. Mebel [b], Ralf I. Kaiser [a,*]

[a] *Department of Chemistry, University of Hawai'i at Manoa, Honolulu, HI 96822, United States*
[b] *Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, United States*

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Abstract

The chemical dynamics of the formation of the *i*-$C_4H_3(X^2A')$ radical together with its partially deuterated isotopomers were investigated in eight crossed molecular beams experiments of dicarbon molecules in their $X^1\Sigma_g^+$ electronic ground and in first excited $a^3\Pi_u$ state with (partially deuterated) ethylene at collision energies between 12.1 and 40.9 kJ mol^{-1}. The center-of-mass angular distributions suggest that the reaction dynamics on the singlet and triplet surfaces are indirect and involve butatriene reaction intermediates. In case of the C_2/C_2H_4 reaction, the 'symmetric' singlet butatriene intermediate would lead solely to a symmetric center-of-mass angular distribution; however, in combination with isotopically labeled reactants, we deduced that triplet butatriene intermediates excited to B/C like rotations likely account for the observed asymmetries in the center-of-mass angular distributions at higher collision energies. The translational energy distributions are also indicative of the involvement of both the triplet and singlet surfaces which lead both to the *i*-$C_4H_3(X^2A')$ radicals through lose (singlet) and tight (triplet) exit transitions states. Also, our experiments helped to determine the enthalpy of formation of the *i*-$C_4H_3(X^2A')$ radical to be about 504 ± 10 kJ mol^{-1} in good agreement with previous computational studies suggesting 498–499 kJ mol^{-1}. The explicit identification of the resonance-stabilized *i*-$C_4H_3(X^2A')$ radical proposes that the reaction of dicarbon with ethylene can lead to formation of *i*-$C_4H_3(X^2A')$ in combustion flames; the *n*-$C_4H_3(X^2A')$ isomer is not formed in this reaction. This conclusion correlates nicely with Hansen's et al. flame experiments at the advanced light source observing only the *i*-$C_4H_3(X^2A')$ radical in hydrocarbon flames.
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Keywords: Combustion chemistry; Reaction dynamics; Crossed beams; Hydrocarbon radicals; Dicarbon

1. Introduction

Small, resonantly stabilized free hydrocarbon radicals have been proposed to be involved in the formation of the first aromatic ring species in combustion flames [1–6] and in the preparation of carbon–carbon composites [7]. Here, the reaction of the *n*-C_4H_3 radical (HCCHCCH) with acetylene (C_2H_2) is thought to lead to the synthesis of the first six-membered aromatic ring in combustion flames, i.e. the phenyl radical (C_6H_5; reaction (1)) [4,8,9]

$$n\text{-}C_4H_3(X^2A') + C_2H_2(X^1\Sigma_g^+) \rightarrow C_6H_5(X^2A') \quad (1)$$

A recent theoretical study by Mebel et al. suggested that reaction intermediates on the C_6H_6 potential energy surface can be either stabilized, isomerize prior to their stabilization to acyclic structures and/or benzene, or fragment via atomic and/or molecular hydrogen loss forming C_6H_5 isomers such as the phenyl radical and C_6H_4 structures like *o*, *m*, *p*-didehydrobenzenes [10]. The authors suggested also the formation of lower mass fragments such as the *n*/*i*-$C_4H_3 + C_2H_3$, channel involving not only the *n*-C_4H_3 radical, but also its *i*-C_4H_3 isomer (H_2CCCCH; X^2A') (Fig. 1). Both the *i*-$C_4H_3(X^2A')$ and the *n*-$C_4H_3(X^2A')$ radicals can be interconverted via atomic hydrogen elimination–addition reactions involving diacetylene (HCCCCH) [11]. The barrier of a hydrogen atom addition to the C2 position of diacetylene forming the *n*-C_4H_3

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[*] Corresponding author.
E-mail address: kaiser@gold.chem.hawaii.edu (R.I. Kaiser).

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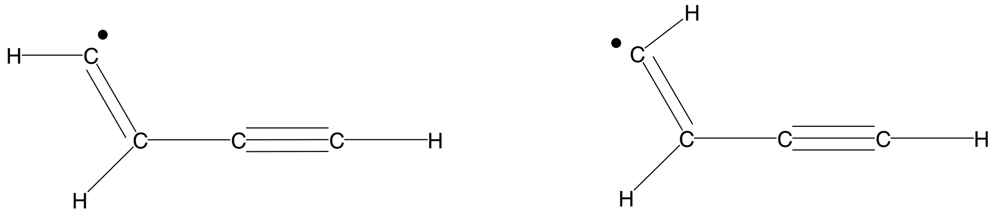
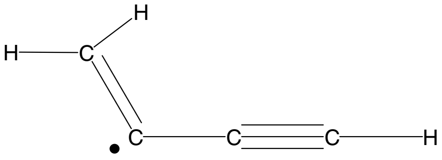


1-butene-3-yne-1-yl (cis n-C_4H_3)

1-butene-3-yne-1-yl (trans n-C_4H_3)



1-butene-3-yne-2-yl (i-C_4H_3)

Fig. 1. Structures of the *cis*/*trans* *n*-C_4H_3 isomers (top) and the *i*-C_4H_3 (bottom).

radical was found to be 28.5 kJ mol^{-1} – higher by about 16 kJ mol^{-1} as that involved in the addition to the terminal carbon atom of the diacetylene molecule leading to the *i*-C_4H_3 isomer. Note that Hansen et al. explicitly observed the *i*-$C_4H_3(X^2A')$ radical in hydrocarbon flames. Based on the ionization potential of 8.06 ± 0.05 eV, the authors derived an enthalpy of formation of 498 ± 4 kJ mol^{-1} at 0 K; this value corresponds nicely with computed enthalpies of formation of 499.4 kJ mol^{-1} (298 K) [11], 499.8 kJ mol^{-1} (298 K) [12], and 498.1 kJ mol^{-1} (0 K) [13]. The corresponding *n*-$C_4H_3(X^2A')$ isomer, which is thermodynamically less stable by 27.6–48.1 kJ mol^{-1} [11–13] was not observed [14]. Recall that the *i*-$C_4H_3(X^2A')$ radical has been observed as a product of the reaction of atomic carbon, $C(^3P_j)$, with allene (H_2CCCH_2) [15] and methylacetylene(CH_3CCH) [16] under single collision conditions. Both the *n*-C_4H_3 and *i*-C_4H_3 isomers have also been inferred as intermediates in the reactions of the ethynyl radical (C_2H) with acetylene [17]; bimolecular collisions of carbon atoms, $C(^3P_j)$, with the propargyl radical (C_3H_3) involve the unimolecular decomposition of the *i*-C_4H_3 structure [18]. Finally, recent crossed beams [19,20] and theoretical studies [21] of the reactions of ground and excited state dicarbon molecules, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$, with ethylene ($C_2H_4$) also suggested that *i*-C_4H_3 can be formed on the singlet and triplet potential energy surfaces, respectively.

However, several features of this reaction have remained hard to pin down so far. First, the previous crossed beams experiments were carried out at a relatively low signal to noise ratio of only 7:1 [19]; this could prevent the identification of the molecular hydrogen elimination channel which electronic structure calculations predicted to exist on the singlet surface [21]. Secondly, the relative importance of the singlet versus triplet surfaces remains to be ascertained. Thirdly, we would like to determine experimentally the enthalpy of formation of the *i*-$C_4H_3(X^2A')$ radical and compare our value with Hansen's data [14]. Finally, our previous investigation could not distinguish to what extent the forward–backward symmetric angular distributions originating from the decomposition of the singlet butatriene intermediates were the result of a long-lived complex or the consequence of a 'symmetric' intermediate (D_{2h}). Here, a 'symmetric intermediate' is defined as a decomposing molecule in which a leaving hydrogen atom can be inter converted by a twofold rotation axis with an equal probability of the hydrogen atom leaving in a direction of $\theta°$ or $\pi–\theta°$; as a result, the center-of-mass angular distribution is forward–backward symmetric although the life-time of the intermediate might be less than its rotation period [22].

To shed light on these open questions, we expanded our previous studies and investigated the collision-energy dependent chemical dynamics of the reaction between dicarbon molecules in their $X^1\Sigma_g^+$ and $a^3\Pi_u$ electronic states with ethylene, $C_2H_4(X^1A_g)$, at four collision energies between 12.1 kJ mol^{-1} and 40.9 kJ mol^{-1}. Here, the collision-energy dependence of the center-of-mass angular distributions is anticipated to gain insights on the involvement of the singlet versus triplet surface. Also, we conducted the reaction with partially deuterated reactants, i.e. $C_2H_3D(X^1A')$, at a selected collision energy of 12.3 kJ mol^{-1} to reduce the symmetry of the singlet butatriene intermediate from D_{2h} to C_s. This is expected to help elucidating to what extent the forward–backward symmetric center-of-mass angular distribution is the effect of the symmetry of the butatriene intermediate or solely from a long-lived complex behavior. Thirdly, crossed beams experiments with three D2-ethylene isotopomers, i.e. $H_2CCD_2(X^1A_1)$, *trans*-$C_2H_2D_2(X^1A_1)$, and *cis*-$C_2H_2D_2(X^1A_1)$, were conducted to investigate the influence of the deuterium substitution and hence reduced symmetry on distinct rotational axis of the decomposing complex(es). Finally, we carried out experiments with $C_2D_4(X^1A_g)$ to