Gas-Phase Synthesis of the Benzyl Radical (C₆H₅CH₂)**
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Abstract: Dicarbon (C₂), the simplest bare carbon molecule, is ubiquitous in the interstellar medium and in combustion flames. A gas-phase synthesis is presented of the benzyl radical (C₆H₅CH₂) by the crossed molecular beam reaction of dicarbon, C₂(X¹Σ⁺, a¹Πₒ) with 2-methyl-1,3-butadiene (isoprene; C₅H₈; X 1A) accessing the triplet and singlet C₇H₈ potential energy surfaces (PEs) under single collision conditions. The experimental data combined with ab initio and statistical calculations reveal the underlying reaction mechanism and chemical dynamics. On the singlet and triplet surfaces, the reactions involve indirect scattering dynamics and are initiated by the barrierless addition of dicarbon to the carbon–carbon double bond of the 2-methyl-1,3-butadiene molecule. These initial addition complexes rearrange via multiple isomerization steps, leading eventually to the formation of C₇H₇ radical species through atomic hydrogen elimination. The benzyl radical (C₆H₅CH₂), the thermodynamically most stable C₇H₇ isomer, is determined as the major product.

Astrochemical and combustion models on the formation of polycyclic aromatic hydrocarbon (PAH) propose molecular weight growth processes through sequential reactions of aromatic (AR) and resonance-stabilized free radicals (RSFR), eventually leading to carbonaceous nanoparticles.[1,2] Along with acetylene, these pathways are considered as the basis for the hydrogen abstraction–acetylene addition (HACA),[3] phenyl addition–cyclization (PAC),[4] ethynyl addition (EA),[5] and vinylacetylene addition (VA)[6] mechanisms. Owing to their stability even at elevated temperatures of several thousand Kelvin, RSFRs and ARs can reach high concentrations in flames and in extraterrestrial environments, such as in circumstellar envelopes of carbon stars. These high concentrations make them important reaction intermediates to be involved in mass growth processes and hence in the formations of PAHs. During the last decade, particular focus has been directed to the role of the C₇H₇ radicals, including benzyl (C₆H₅CH₂), o-, m-, and p-tolyl (2-, 3-, and 4-tolyl; C₅H₈CH₃), and cycloheptatrienyl (C₇H₇) radicals (Scheme 1).[7-9] The benzyl radical (C₆H₅CH₂) has been proposed to yield indene (C₅H₈) upon reaction with acetylene (C₂H₂).[10,11] Indene may further produce indenyl radical(s). These indenyl radical(s) may then react with vinylacetylene (C₅H₅) to lead to fluorene, 1H-benz[f]indene, 1H-benz[g]indene, and/or 1H-phenalen. Owing to the potential key role of the benzyl (C₆H₅CH₂) radical, which is both aromatic and resonantly stabilized, in the formation of PAHs carrying five-membered rings, reaction mechanisms to distinct C₇H₇ isomers involving the phenyl radical (C₆H₅), fulvenallene (C₇H₆), 1-ethynyl-cyclopentadiene (C₅H₈), and the propargyl radical (C₅H₇) have been explored computationally.[7,8,12,13] However, the formation of C₇H₇ isomers (among them the thermodynamically most stable benzyl (C₆H₅CH₂) radical) via the bimolecular reaction of ubiquitous dicarbon molecules (C₂) with C₇H₈ isomers such as 2-methyl-1,3-butadiene (isoprene, C₅H₈; X 1A) has never been reported. The dicarbon molecule is abundant in hydrocarbon flames and in the interstellar medium while the 2-methyl-1,3-butadiene can be formally derived from 1,3-butadiene (C₅H₆) by replacing the hydrogen atom at the C2 carbon atom by a methyl group. The 1,3-butadiene, together with its C₅H₆ isomers 1,2-butadiene, 1-butyne, and 2-butyne, is omnipresent in combustion flames, such as of ethylene and cyclohexane. Furthermore, C₅H₈ isomers have been probed in hydrocarbon flames, where the benzyl (C₆H₅CH₂) radical is determined as the major C₇H₇ species. Because of its resonant and aromatic stabilization, benzyl reaches significant concentrations in combustion flames and thus an understanding of its chemistry, in particular its formation and decomposition processes as well as bimolecular reactions, is essential for the development of accurate and predictive combustion engine models. Herein, we report the results of crossed molecular beams reaction of dicarbon with 2-methyl-1,3-butadiene accessing various
chemically activated reactive intermediates on the singlet and triplet \( \text{C}_2\text{H}_2 \) surfaces, which then decompose to products including distinct \( \text{C}_2\text{H}_4 \) isomers. These systems are also interesting from the viewpoint of a physical–organic chemist as they are benchmarks to unravel the chemical reactivity, bond breaking processes, and the synthesis of truly combustion and astrochemically relevant cyclic and aromatic hydrocarbon radicals from acyclic precursors via bimolecular gas-phase reactions in single collision events.

Reactive scattering signal from the reactions of dicarbon (\( \text{C}_2; 24 \text{ amu} \)) with 2-methyl-1,3-butadiene (\( \text{C}_5\text{H}_8; 68 \text{ amu} \)) was observed at \( m/z = 91 \) (\( \text{C}_2\text{H}_4^+ \)), \( m/z = 90 \) (\( \text{C}_4\text{H}_6^+ \)) and \( m/z = 89 \) (\( \text{C}_5\text{H}_7^+ \)) with data at \( m/z = 89 \) depicting the best signal-to-noise ratio. The time-of-flight (TOF) spectra at these mass-to-charge ratios were superimposable after scaling, suggesting that signal at \( m/z = 89 \) and 89 originated from dissociative ionization of the \( \text{C}_2\text{H}_4 \) product in the electron impact ionizer of the detector; if TOF data at two mass-to-charge ratios (\( m/z \)) are overlapping, data at lower \( m/z \) are fragments from higher \( m/z \). Therefore, our data suggest that only the dicarbon versus atomic hydrogen exchange channel is open, and that the molecular hydrogen loss pathways are closed. It should be emphasized that apart from dicarbon, the primary beam also contains atomic carbon and tricarbon molecules; however, tricarbon is unreactive with isoprene and hence does not interfere with the scattering signal obtained at lower mass-to-charge ratios. This is evident from the lack of any reactive scattering signal at \( m/z = 91 \) and 90 originated from dissociative ionization of the \( \text{C}_2\text{H}_4 \) product with the \( \text{C}_5\text{H}_7 \) isomers. These systems are also interesting from the viewpoint of a physical–organic chemist as they are benchmarks to unravel the chemical reactivity, bond breaking processes, and the synthesis of truly combustion and astrochemically relevant cyclic and aromatic hydrocarbon radicals from acyclic precursors via bimolecular gas-phase reactions in single collision events.

Figure 1. Time-of-flight data (a) and laboratory angular distribution (b) at \( m/z = 89 \) (\( \text{C}_7\text{H}_7^+ \)) for the reaction of dicarbon (\( \text{C}_2 \)) with isoprene (\( \text{C}_5\text{H}_8 \)) forming \( \text{C}_7\text{H}_7 \) product(s) at collision energy of 42.7 ± 1.5 kJ mol\(^{-1} \). The circles represent the experimental data, error bars present the standard deviation, and the solid lines represent the fit.

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symmetric with respect to 90° and is distributed over the complete angular range of 0° to 180°. This finding suggests that this reaction follows indirect scattering dynamics via the formation of C2H,4 reaction intermediate(s). Also, the distribution maximum of the center-of-mass angular distribution at 90° indicates “sideways scattering,” that is, the departing atomic hydrogen atom is emitted preferentially perpendicularly with respect to the rotational plane of the decomposing complex. This finding is also reflected in the flux contour map (see the table of contents graphic).

Second, we also explored the reaction of singlet and triplet dicarbon with isoprene computationally; the singlet and triplet C2H,4 potential energy surfaces (PESs) are presented in Figure 3 and Figure 4. Considering the singlet surface, dicarbon can add without an entrance barrier to either the C3–C4 or the C1–C2 carbon–carbon double bonds of isoprene, yielding intermediates si1 and si2, respectively. These collision complexes ring open to si3 and si4, respectively. Both acyclic intermediates may undergo hydrogen shifts, yielding eventually intermediate si5, which then undergoes a trans–cis conversion to si6 through a low barrier of only 21 kJ mol⁻¹. A hydrogen shift in the latter yields si7, which subsequently isomerizes via cis–trans conversion to si8. This intermediate can undergo ring closure to si9 or si10; the ring closure to the former is initiated with a 1,3–H atom shift from the methyl group. Considering the inherent barriers of 340 and 145 kJ mol⁻¹, the formation of si10 should be preferential. This species depicts a hydrogen shift at the ring from the para to the meta position to si11, with the latter isomerizing via yet another hydrogen migration to si12 (toluene). Toluene is the global minimum on the C2H,4 potential energy surface and can undergo unimolecular decomposition involving atomic hydrogen loss via four simple bond-rupture processes. These form the benzyl radical (C6H5CH2) and/or α-, m-, and/or p-tolyl radicals. The benzyl radical is thermodynamically more stable by about 94 kJ mol⁻¹ compared to the tolyl radicals due to resonance stabilization of the radical center. Note that si1 and si2 can also react to products other than C2H,4 (Supporting Information, Figure S1).

Figure 4 shows the reaction paths for addition of triplet dicarbon to the isoprene. The triplet dicarbon can add without entrance barrier to the C4 and C1 carbon atoms of isoprene, yielding intermediates ti1 and ti2, respectively, which are bound by 180 and 190 kJ mol⁻¹ with respect to the separated reactants. These intermediates isomerize via hydrogen shifts and ring closures involving ti3, ti6, ti11, ti12, and ti13 to eventually form the cyclic structures ti4, ti7, ti8, and ti10. Considering the inherent barriers to isomerization, all isomerization pathways involving ti3 and ti12 yield ti4, with ti7 leading to ti10 and ti8. What is the fate of these cyclic intermediates? Intermediate ti6 isomerizes via hydrogen shift to ti5, which then decomposes to the benzyl radical through a tight exit transition state located 16 kJ mol⁻¹ above the separated products. ti8 and ti10 preferentially decompose by atomic hydrogen losses yielding m- and p-tolyl radicals, respectively, or undergo distinct hydrogen shifts (via ti9) and then dissociate to the benzyl radical (C6H5CH2) and/or α-, m-, and/or p-tolyl radicals, or phenyl plus the methyl radical (CH3). Note that with the exception of the decomposition of ti9 to the benzyl radical, all exit transition states are tight. Intermediates ti1 and ti2 can also decompose to acyclic products (Supporting information Figure S1); however, these pathways are energetically not favorable.

Having interpreted the experimental data and the potential energy surfaces, the experimental findings (reaction energies, exit barriers, indirect nature of the reaction mechanism, and geometry of the exit transition state) can be merged with the computational data. A comparison of the experimentally determined exoergicity of the reaction of dicarbon with 2-methyl-1,3-butadiene of 474 ± 32 kJ mol⁻¹ with the computed reaction energies (477 ± 10 kJ) suggests the formation of at least the thermodynamically most stable C2H,4 isomer: the benzyl radical (C6H5CH2). Considering that the experimentally determined off-zero peaking at 20 to 30 kJ mol⁻¹ of the center-of-mass translational energy distribution suggests a tight exit transition state, the computational data propose that at least one decomposition pathway involves ti5. In this case, ti5 undergoes hydrogen loss via a barrier located 16 kJ mol⁻¹ above the separated products; the unimolecular decomposition of ti9 is barrierless and thus not expected to result in an off-zero peaking of the center-of-mass translational energy distribution. How can ti5 be formed? Considering the triplet surface, ti5 is most likely reached from ti1 via ti3 and ti4 or from ti2 via ti11, ti12, and ti4 involving hydrogen migrations and cyclization. Based on these considerations, we can conclude that on the triplet surface, triplet dicarbon adds to the C4 or C1 carbon atom of 2-methyl-1,3-butadiene, yielding intermediates ti1 and ti2, respectively. Intermediate ti1 undergoes hydrogen migration to form ti3, which then ring-closes to ti4. Alternatively, ti2 features a hydrogen shift to ti11 followed by rotation around
a C–C bond (to \textit{ti12}) and a ring closure to \textit{ti4}. This intermediate undergoes yet another hydrogen migration to \textit{ti5}, which ultimately eliminates atomic hydrogen to form the benzyl radical. These indirect scattering dynamics were also predicted based on the center-of-mass angular distribution. Finally, recall that based on the center-of-mass angular distribution, the exit transition state was suggested to hold geometrical constraints depicting a hydrogen atom loss almost perpendicularly to the rotating plane of the decomposing complex. This finding was also confirmed computationally, predicting an angle of the hydrogen elimination of 81.3° (Figure 5).

Note that based on the experimentally derived energetics alone, we cannot rule out the formation of thermodynamically less stable C7H7 radicals. Our statistical RRKM calculations predict that upon dicarbon addition to C1 under our experimental conditions, the benzyl radical dominates and is formed at fractions of about 61% with tolyl radicals contributing to about 37% with nearly equal contributions of \textit{m}- and \textit{p}-tolyl; furthermore, non-aromatic products are minor and contribute only 2%. Adding dicarbon to C4 produces about 25% benzyl and 75% \textit{m}- and \textit{p}-tolyl. The higher yield of benzyl computed for the C1 addition is determined by the fact that the barrier for the \textit{ti2}→\textit{ti11} isomerization eventually leading to \textit{ti4} is 20 kJ mol\(^{-1}\) lower than that for the competing \textit{ti2}→\textit{ti13} process, whereas the barriers for \textit{ti1}→\textit{ti3} on the path to \textit{ti4} and \textit{ti1}→\textit{ti6} are nearly equal. If the C1 and C4 additions are equally split, we expect about 43% of benzyl.

The computations predict further that on the singlet surface, the addition to the C3–C4 and C1–C2 may eventually yield (via the collision complexes \textit{si1} and \textit{si2}) \textit{si8} via a multi-step isomerization sequence involving successive hydrogen shifts. Considering the barrier to isomerization, intermediate \textit{si8} is expected to rearrange to \textit{si10}, which eventually yields singlet toluene (\textit{si12}). The latter is expected to decompose via loose exit transition states to the benzyl as well as tolyl radicals, with a benzyl being formed preferentially. However, before intermediate \textit{si8} can be even formed, the reaction can alternatively proceed by numerous fragmentation channels involving \textit{H}, CH\(_3\), and C\(_3\)H\(_3\) elimination and the production of non-aromatic radicals (Supporting Informa-
tion, Figure S1). We conclude therefore that the addition of singlet dicarbon to the C3–C4 bond of 2-methyl-1,3-butadiene most likely forms non-aromatic CH2CCCHCH2 plus methyl and sp2–sp4 plus atomic hydrogen and the pathway from si3 to the aromatic products is effectively closed. For si4, the barrier for the H shift to form si5 is 292 kJ mol⁻¹. 46 and methyl-1,3-butadiene should be less than 21%.

In summary, by merging the experimental and computational data, we provided compelling evidence that on the triplet surface the thermodynamically most stable aromatic and resonantly stabilized free radical benzyl is formed preferentially. This reaction provides a barrierless and
hitherto overlooked reaction pathway via a single collision event from acyclic, non-aromatic reactants. As the reaction has no entrance barrier, is exoergic, and all transition states involved are located below the energy of the separated reactants, the reaction of triplet dicarbon with isoprene may form benzyl radical not only in high-temperature combustion flames, but also in low temperature astrochemical environments. On the other hand, on the singlet surface, the benzyl radical is expected to be of minor importance. Further, the replacement of a hydrogen atom by a methyl group in the 1,3-butadiene reactant leads to an active participation of the methyl group in the reaction dynamics to form the benzyl radical and not just purely a spectator. Therefore, reactions of simple C1 to C3 combustion relevant radicals are expected to follow a unique chemistry once reacting with methyl- and even alkyl-substituted reactants, which is anticipated to be remarkably distinct from their non-alkyl substituted counterparts.

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