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Reaction Dynamics of Phenyl Radicals (C_6H_5) with Propylene (CH_3CHCH_2) and Its Deuterated Isotopologues

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Received: November 23, 2007; In Final Form: January 11, 2008

The reactions between phenyl radicals (C_6H_5) and propylene (CH_3CHCH_2) together with its D6- and two D3-isotopologues were studied under single collision conditions using the crossed molecular beams technique. The chemical dynamics inferred from the center-of-mass translational and angular distributions suggests that the reactions are indirect and initiated by an addition of the phenyl radical to the α-carbon atom (C1 carbon atom) of the propylene molecule at the $=CH_2$ unit to form a radical intermediate ($CH_3CHCH_2C_6H_5$) on the doublet surface. Investigations with D6-propylene specified that only a deuterium atom was emitted; the phenyl group was found to stay intact. Studies with 1,1,2-D3- and 3,3,3-D3-propylene indicated that the initial collision complexes $CH_3CDCD_2C_6H_5$ (from 1,1,2-D3-propylene) and $CD_3CHCH_2C_6H_5$ (from 3,3,3-D3-propylene) eject both a hydrogen atom via rather loose exit transition states to form the D3-isotopomers of *cis*/*trans*-1-phenylpropene ($CH_3CHCHC_6H_5$) (80−90%) and 3-phenylpropene ($H_2CCHCH_2C_6H_5$) (10−20%), respectively. Implications of these findings for the formation of polycyclic aromatic hydrocarbons (PAHs) and their precursors in combustion flames are discussed.

1. Introduction

In recent years, an investigation of the C_9H_{10} potential energy surface (PES) has received considerable attention both from the experimental and theoretical viewpoints. This is because C_9H_{10} isomers such as indane, α-methylstyrene, and *cis*/*trans*-1-phenylpropene are considered as important reaction intermediates and toxic byproducts in the combustion of fossil fuel in diesel[1] and jet engines,[2] in the thermal degradation of polymers,[3,4] in organic waste incineration,[5] and in cigarette smoke.[6] Since the phenyl group presents a dominating building block of precursor molecules to synthesize polycyclic aromatic hydrocarbons (PAHs), various reaction models have been proposed regarding how these molecules can be formed in combustion flames.[7−9] These kinetic models predict that the phenyl radical, $C_6H_5(X^2A_1)$, represents one of the most significant transient species to initiate the formation of PAHs. These networks propose further that reactions of phenyl radical with unsaturated hydrocarbon molecules such as (substituted) acetylenes, olefins, and aromatic molecules proceed via addition of the phenyl radical to the π electronic system of the unsaturated coreactant. This initial addition complex—depending on the collision rates—either fragments to the initial reactants, decomposes via atomic hydrogen loss(es), isomerizes prior to their decomposition, and/or is stabilized at higher pressures if the lifetime of the intermediate is longer than the time scale necessary to divert the internal energy of the complex via a third body collision.[10−14] Due to the importance of phenyl radical reactions, we have investigated in our laboratory the reaction dynamics of phenyl radicals with acetylene (C_2H_2),[15] ethylene (C_2H_4),[16] methylacetylene (CH_3CCH),[17] allene (H_2CCCH_2),[17] and benzene (C_6H_6)[18] together with their (partially) deuterated isotopologues in crossed beam experiments leading to the formation of phenylacetylene (C_6H_5CCH), styrene ($C_6H_5CHCH_2$), 1-phenylmethylacetylene ($CH_3CCC_6H_5$), 1-phenylallene ($C_6H_5HCCCH_2$), and biphenyl ($C_6H_5C_6H_5$) at collision energies in the range of 71−185 kJ mol^{-1}. These studies showed that (i) the phenyl group stayed intact, (ii) the energy randomization is likely incomplete, and (iii) the reaction dynamics are indirect and dominated by atomic hydrogen loss pathways.

Here, we expand these studies and investigate the reaction dynamics of phenyl radicals with propylene (CH_3CHCH_2). Note that previous studies on the phenyl−propylene systems are sparse. In 1972, Hefter and co-workers[19] studied the reaction of phenyl radicals with propylene in liquid propylene at 183 K utilizing electron spin resonance. They concluded that the reaction is initiated by an addition of the phenyl radical to the $=CH_2$ group of propylene; in the liquid phase, the authors also observed the $C_6H_5CH_3CHCH_2$ radical formed via addition of phenyl to the β-carbon atom of propylene and the allyl radical as an abstraction product. Recently, Park et al. followed the kinetics of this reaction by cavity ring-down spectroscopy at temperatures between 296 and 496 K.[20] The reaction rate was derived to be $10^{11.93\pm0.06} \times e^{(-1512\pm51)/T}$ cm^3 s^{-1}. Similar to Hefter et al., Park et al. concluded, with the help of electronic structure calculations, that the phenyl radical adds to the $=CH_2$ unit of the propylene molecule. However, reaction products are still elusive. In our crossed beam studies, by using partially deuterated reactants, we will pin down to what extent the hydrogen atom is emitted from the

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10.1021/jp711146a CCC: $40.75

TABLE 1: Peak Velocities (v_p), Speed Ratios (S), Center-of-Mass Angles (Θ_{CM}), and the Collision Energies of the Phenyl Radical with the Reactants (E_c) of the Segments Crossing at the Interaction Region

beam	v_p, ms^{-1}	S	E_c, kJ mol^{-1}	Θ_{CM}
$C_6H_5(X^2A_1)$/He	2981 ± 92	4.9 ± 0.3	–	–
$CH_3CHCH_2(X^1A')$	835 ± 25	12.5 ± 1.0	130.2 ± 8.2	8.7 ± 0.5
$C_6H_5(X^2A_1)$/He	3525 ± 54	5.5 ± 0.5	–	–
$CD_3CHCH_2(X^1A')$	820 ± 25	12.5 ± 1.0	186.0 ± 6.0	7.7 ± 0.3
$C_6H_5(X^2A_1)$/He	3525 ± 54	5.5 ± 0.5	–	–
$CH_3CDCD_2(X^1A')$	820 ± 25	12.5 ± 1.0	186.0 ± 6.0	7.7 ± 0.3
$C_6H_5(X^2A_1)$/He	3525 ± 54	5.5 ± 0.5	–	–
$CD_3CDCD_2(X_1A')$	820 ± 25	12.5 ± 1.0	193.6 ± 6.3	8.3 ± 0.4

methyl group or from the olefinic vinyl unit (or both). This allows us to extract branching ratios of the reaction products. In addition, an expansion of the reactant from methylacetylene to propylene by adding two hydrogen atoms increases the degrees of freedom by six. Therefore, our studies also aim to investigate the influence of these additional degrees of freedom on the lifetime of the reaction intermediates and, hence, on the energy randomization in the activated complex(es).

2. Experimental Section

The experiments were carried out in a crossed molecular beam machine at The University of Hawai'i under single collision conditions.[21] A pulsed supersonic beam of phenyl radicals was generated via flash pyrolysis of the nitrosobenzene precursor (C_6H_5NO, Aldrich) in the primary source chamber at seeding fractions of less than 0.1% by operating a modified Chen source at 200 Hz.[22,23] Helium gas (3040 Torr, 99.9999%; Matheson) was introduced into a stainless steel reservoir that was kept at 283 K. The mixture was expanded at a backing pressure of 920 Torr through a resistively heated silicon carbide tube estimated to be at 1200−1500 K. At these experimental conditions, the decomposition of the nitrosobenzene molecule was quantitative; all nitroso benzene molecules dissociated to phenyl radicals plus NO molecules. After passing a skimmer, a four-slot chopper wheel selected a part of the phenyl radical beam; the peak velocities and speed ratios of the segments of the beams crossing the hydrocarbon beam in the interaction region are compiled in Table 1. This phenyl radical beam intersected pulsed propylene (CH_3CHCH_2, Aldrich; 99+ %), D6-propylene (CD_3CDCD_2, CDN; 99+ % D), 3,3,3-D3-propylene (CD_3CHCH_2, CDN; 99+ % D), and 1,1,2-D3-propylene (CH_3CDCD_2, CDN; 99+ % D) beams released by a second pulsed valve at 550 Torr backing pressure under well-defined collision energies in the interaction region.

The reactively scattered products were probed using a quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron-impact ionization of the molecules at 90 eV at an emission current of 2 mA. The detector could be rotated within the plane defined by the primary and the secondary reactant beams to take angular resolved TOF spectra. By integrating the TOF spectra at the laboratory angles and correcting for the day-to-day intensity fluctuations of the phenyl radical beam, the laboratory angular distribution, which depicted the integrated signal intensity of an ion of distinct m/z versus the laboratory angle, could be obtained. Information on the chemical dynamics was gained by fitting these TOF spectra and the angular distribution in the laboratory frame (LAB) using a forward-convolution routine.[24−26] This approach initially assumed an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the center-of-mass reference frame (CM). TOF spectra and the laboratory angular distribution were then calculated from these center-of-mass functions. This plot contains all the basic information on the reactive scattering process. Since previous kinetics studies of phenyl radical reactions with propylene showed the existence of a threshold energy to reaction, E_o,[20] we included an energy-dependent cross section, $\sigma(E_c) \sim (1 - E_o/E_C)$, via the line-of-center model with the collision energy E_C for $E_C \geq E_o$ in the fitting routine.[27] Due to the low signal counts, we had to record up to 3×10^6 TOF spectra to obtain a reasonable signal-to-noise ratio of the reactively scattered species. This limited us to carry out the experiments with the deuterated propylene reactants only at the corresponding center-of-mass angles.

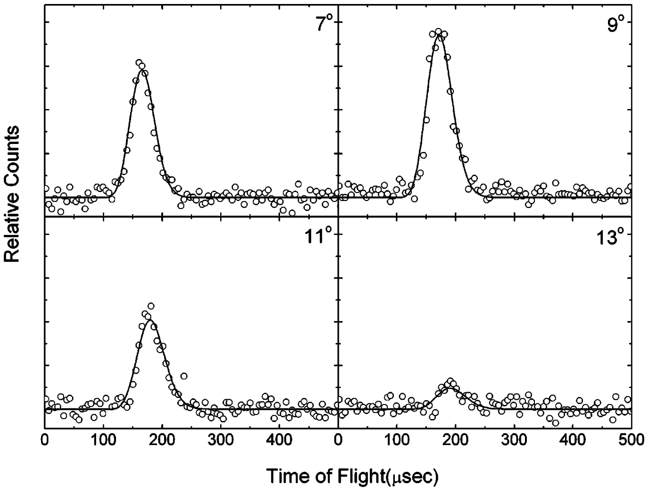

Figure 1. Selected time-of-flight data recorded at a mass-to-charge (m/z) of 118 ($C_9H_{10}^+$) in the reaction of phenyl radicals with propylene at a collision energy of 130.2 kJ mol^{-1}. The open circles are the experimental data and the solid lines the fits.

3. Results

3.1. Laboratory Data. We recorded reactive scattering signal at mass to charge ratios from $m/z = 118$ ($C_9H_{10}^+$) (Figure 1) down to $m/z = 114$ ($C_9H_6^+$). TOF spectra recorded at lower m/z ratios showed identical pattern and could be fit with identical center-of-mass functions as those data taken at $m/z = 118$. This suggests that signals in the range of $m/z = 117-114$ originated from dissociative ionization of the C_9H_{10} parent molecule in the electron impact ionizer of the detector. Also, we can deduce that in the reaction of the phenyl radical with propylene, the phenyl radical versus atomic hydrogen exchange pathway is open. Besides the atomic hydrogen loss, we also investigated a possible methyl group (CH_3) loss channel. This was achieved by monitoring ion counts at $m/z = 104$ ($C_8H_8^+$). Nevertheless, no reactive scattering signal from the $C_8H_8 + CH_3$ pathway could be observed. In contrast to the hydrogen atom loss channel, it is more difficult to observe the methyl loss pathway, simply because the corresponding Newton sphere of the methyl group loss is larger compared to the atomic hydrogen loss channel. Accounting for the data accumulation time at $m/z = 118$ vs 104 and the signal-to-noise ratio of our experiments, we can estimate that the upper limits of the importance of the methyl loss pathway is 10%. It should be mentioned that we also monitored the signal at $m/z = 119$. Considering the intensity of the signal of about 10−15% compared to $m/z = 118$ and—after scaling—the identical shape of the TOFs of $m/z = 118$ and $m/z = 119$, we can conclude that signal at $m/z = 119$ originated from $^{13}CC_8H_{10}^+$. Figure 2 visualizes the laboratory angular (LAB) distribution of the ion counts at $m/z = 118$. Obviously,

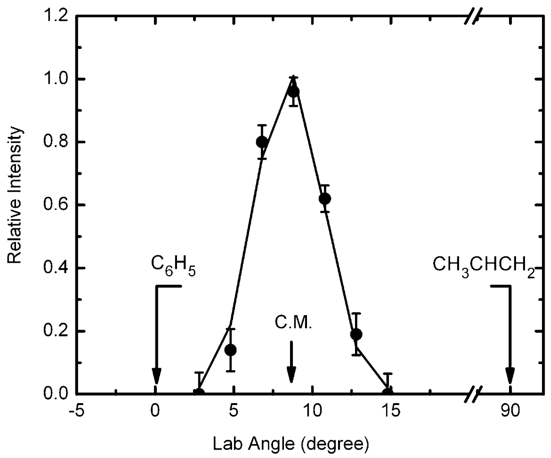

Figure 2. Laboratory angular distribution of ion counts recorded at a mass-to-charge (*m*/*z*) of 118 ($C_9H_{10}^+$) in the reaction of phenyl radicals with propylene at a collision energy of 130.2 kJ mol^{-1}. The circles are the experimental data and the solid lines the fits. C.M. defines the center-of-mass angle.

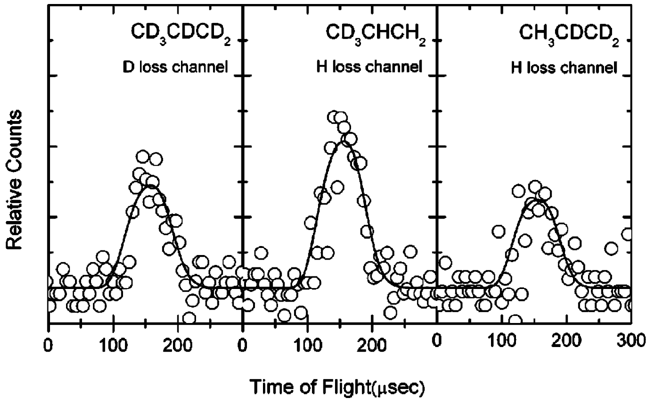

Figure 3. Time-of-flight spectra of mass-to-charge (*m*/*z*) of 123 ($C_9H_5D_5^+$) (left), 121 ($C_9H_7D_3^+$) (center), and 121 ($C_9H_7D_3^+$) (right) recorded during the reactions of phenyl radicals with isotopically substituted propylene molecules at the corresponding center-of-mass angles. The open circles are the experimental data and the solid lines the fits. Fits of the signal of *m*/*z* = 121 ($C_9H_7D_3^+$) (right) have been obtained with a center-of-mass translational energy distribution as depicted in Figure 4, but cut at the high energy end by 20 kJ mol^{-1}.

the LAB distribution is very narrow and spreads only over about 13° in the scattering plane defined by both supersonic beams. In addition, the LAB distribution is slightly forward peaked with respect to the primary beam.

To gather information on the position of the hydrogen loss (phenyl versus methyl group versus vinyl hydrogen atoms), we conducted reactions of the phenyl radical (C_6H_5) with D6-propylene. In the case of a hydrogen atom ejection, signal should be observable at *m*/*z* = 124 ($C_9H_4D_6^+$); if a deuterium atom elimination happens, we should be able to monitor ion counts at *m*/*z* = 123 ($C_9H_5D_5^+$). In principle, *m*/*z* = 123 can also originate from fragmentation of *m*/*z* = 124. In our crossed beam study, we detected signal at *m*/*z* = 123 for the reactions of phenyl radicals with D6-propylene (Figure 3). Within the signal-to-noise limit, we could not detect any ion counts at *m*/*z* = 124. This suggests that only the deuterium atom is being released; the phenyl group is likely to be conserved in the reaction. Consequently, in the reaction of phenyl radicals with propylene, atomic hydrogen is released from the propylene reactant.

However, we should stress that the hydrogen atom can be released either from the vinyl or from the methyl group of the propylene molecule (or from both). To pin down the ultimate pathway(s), we conducted crossed beam experiments of phenyl radicals with 3,3,3-D3-propylene (CD_3CHCH_2) and 1,1,2-D3-propylene (CH_3CDCD_2). Let us consider the phenyl−3,3,3-D3-propylene reaction first. If a hydrogen atom is emitted from the vinyl group, signal should be observable at *m*/*z* = 121 ($C_9H_7D_3^+$); if a deuterium atom ejection takes place, ion counts at *m*/*z* = 120 ($C_9H_8D_2^+$) should be detectable. Also, signal at *m*/*z* = 120 can arise from fragmentation of $C_9H_7D_3^+$. On the other hand, let us consider now 1,1,2-D3-propylene. Here, if atomic hydrogen is emitted from the methyl group, signal should be detectable at *m*/*z* = 121 ($C_9H_7D_3^+$); however, if an atomic deuterium is ejected from the vinyl group, it should be feasible to probe ion counts at *m*/*z* = 120 ($C_9H_8D_2^+$). Similar to the reaction of phenyl radicals with 3,3,3-D3-propylene, the signal at *m*/*z* = 120 may originate from fragmentation of $C_9H_7D_3^+$. On the basis of these considerations, if the signal at *m*/*z* = 121 is observed in the reactions of phenyl radicals with 3,3,3-D3-propylene and 1,1,2-D3-propylene, this should be a unique indicator of a hydrogen atom loss from the vinyl and methyl groups, respectively. As a matter of fact, we observed a signal at *m*/*z* = 121 for the 3,3,3-D3-propylene *and* 1,1,2-D3-propylene reactants (Figure 3). Therefore, we can conclude that two hydrogen elimination pathways exist: from the vinyl group and from the methyl group. We would like to stress that the use of perdeuterated and partially deuterated reactants only allowed us to record TOF spectra at the corresponding center-of-mass angles due to the low signal counts and the costs of these chemicals.

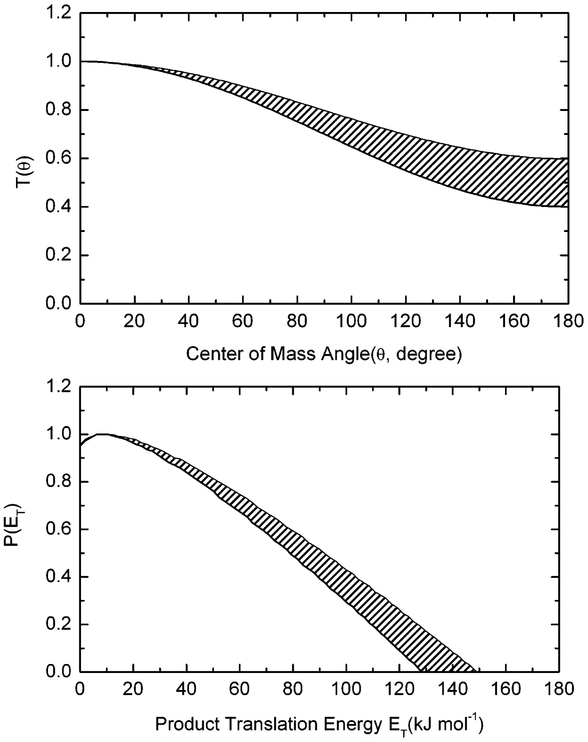

Figure 4. Center-of-mass translational (lower) and angular distributions (upper) of the C_9H_{10} product(s) formed in the reaction of phenyl radicals with propylene. The hatched areas account for the experimental error limits of the laboratory angular distribution as well as the peak velocity and speed ratio (Table 1).

3.2. Center of Mass Translational Energy, *P*(*E*$_T$), and Angular Distribution, *T*(*θ*). As evident from the center-of-mass functions (Figure 4), a reasonable fit of the TOF data (Figure 1) and LAB distribution (Figure 2) of the phenyl−propylene reaction could be achieved with a single reaction channel leading to a product of the molecular formula C_9H_{10}

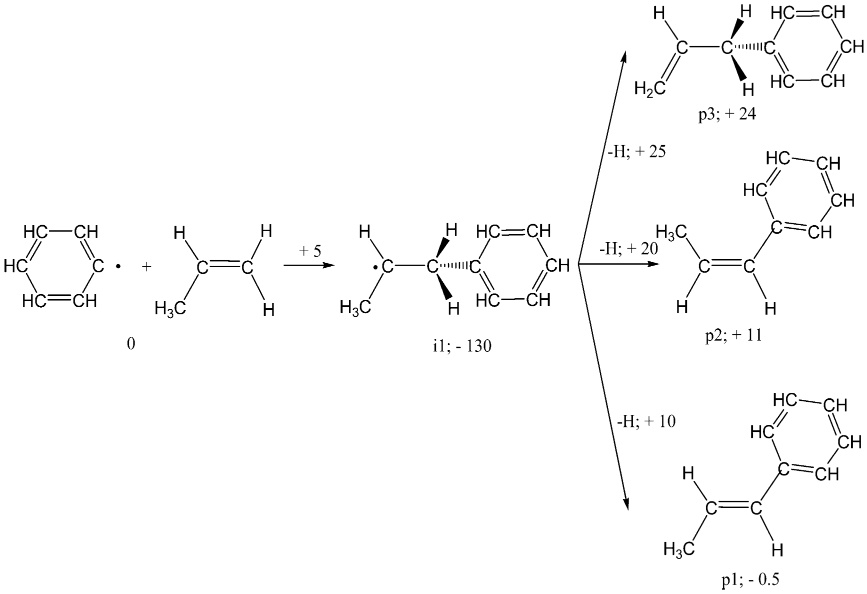

Figure 5. Schematic representation of the reaction of phenyl radicals with propylene. The energies (in kJ mol^{-1}) of the intermediates, transition states, and products were taken from ref 20 and are given with respect to the separated reactants.

plus atomic hydrogen. Best fits of the center-of-mass translational energy distributions, $P(E_T)$s, were achieved with distributions extending to maximum translational energy releases, E_{max}, of 140 ± 10 kJ mol^{-1}. Recall that this high-energy cutoff, which resembles the sum of the absolute of the reaction energy plus the collision energy, permits us to gauge the reaction energy. This suggests that the reaction energy of phenyl radicals with propylene leading to $C_9H_{10} + H$ is about -10 ± 10 kJ mol^{-1}. Therefore, the reaction could be—within the error limits—thermoneutral, but it is most likely slightly exoergic. Finally, the $P(E_T)$ is very broad and shows a significant distribution maximum of about 10 kJ mol^{-1}, i.e. a peak slightly away from zero translational energy. The peaking close to zero translational energy indicates that the reaction of the phenyl radicals with propylene involves a rather loose exit transition state.[28,29]

The center-of-mass angular distribution assists to collect supporting information on the reaction dynamics. Here, the angular flux distribution is asymmetric and shows intensity over the complete angular range from 0° to 180° and enhanced flux in the forward hemisphere (with respect to the phenyl radical beam) is clearly evident. These data suggest that the reaction follows indirect scattering dynamics via formation of a C_9H_{11} complex and that the lifetime of the C_9H_{11} intermediate(s) is shorter than the rotational period of the reaction intermediate(s) (osculating complex).[30] We would like to stress that, despite the unfavorable kinematics of the reaction, the data obtained within the error limits from the $T(\theta)$ distribution depict clearly that the center-of-mass angular distribution is forward scattered with respect to the phenyl radical beam; no acceptable fit could be obtained with forward−backward symmetric and/or isotropic distributions. Remember that our fits incorporated an energy-dependence of the threshold energy (section 2); our fits were relatively insensitive within the range of threshold energies to the reaction of 5 and 30 kJ mol^{-1}.

4. Discussion

4.1. Energetical Considerations. On the basis of the energetics of the reactions, we are attempting now to elucidate the product isomer(s) formed in the reactions of phenyl radicals with propylene. The center-of-mass translational energy distribution for the atomic hydrogen loss channel indicated that the reaction energy is about -10 ± 10 kJ mol^{-1}. We can compare this data with computed reaction energies of possible products (Figure 5).[20] Here, the reaction energy can account for the formation of the *cis*/*trans*-1-phenylpropylene (*cis*/*trans*-CH_3-$CHCHC_6H_5$) isomer (**p1/p2**). However, on the basis of the energetics alone, we cannot elucidate the importance of the less stable product isomer, **p3**, and we have to combine the data on the energetics with the results obtained from the reaction of phenyl radicals with distinct isotopologues of propylene. However, we should stress that the formation of the thermodynamically most stable C_9H_{10} isomer, indane, is exoergic by 50 kJ mol^{-1};[31] therefore, the synthesis of this structure can be likely ruled out. It should be stressed that, in the reaction of phenyl radicals with D6-propylene, no atomic hydrogen loss pathway was observed. Since the formation of indane should involve hydrogen shifts and an emission of a hydrogen atom (Figure 7), the failed detection of the atomic hydrogen loss pathway in the reaction of phenyl with D6-propylene presents a more direct proof that indane is not synthesized. Under the assumption that *cis*/*trans*-1-phenylpropylene is the dominating reaction product, we can compute that the fraction of the total available energy channeling into the translational degree of the reaction products is 35 ± 8%.

4.2. Proposed Reaction Dynamics. We are combining now the experimental results extracted from the laboratory data and from the center of mass functions in an attempt to explain the most likely reaction dynamics in the phenyl−propylene system. First, we correlate the structure of the *cis*/*trans*-1-phenylpropylene (*cis*/*trans*-$CH_3CHCHC_6H_5$) product (**p1/p2**) with the geometry of the propylene (CH_3CHCH_2) and phenyl radical (C_6H_5) reactants (Figure 5). Here, we recommend that the phenyl radical adds with the radical center to the α-carbon of the propylene molecule holding the $=CH_2$ unit. This attack position is likely directed by two factors. First, the sterical hindrance of the methyl group reduces the cone of acceptance of addition of the phenyl radical to the β-carbon atom of the propylene molecule. Second, the phenyl radical is an electron-deficient reactant and attacks preferentially the carbon atom with the highest electron density. In propylene, the α, β, and γ (methyl group) have charges of −0.42, 0.0, and −0.41.[32] On the basis of the sterical hindrance of the β-attack and the enhanced

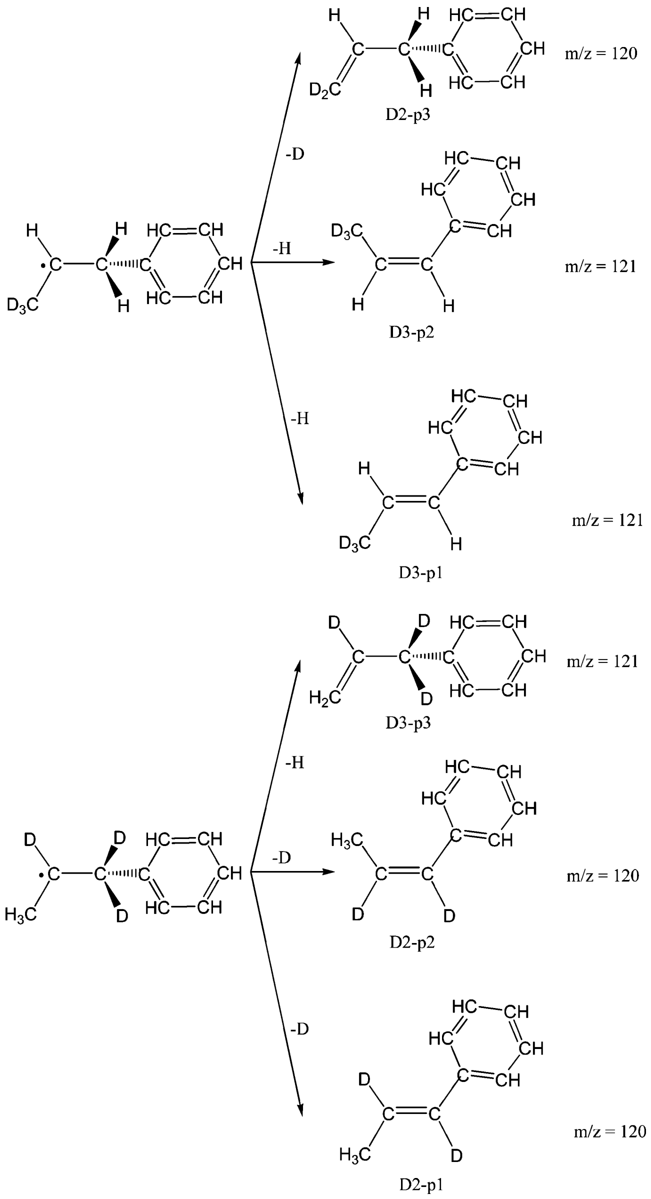

Figure 6. Schematic representation of the decomposition of intermediate **i1** formed in the reactions of reactions of phenyl radicals with 1,1,2-D3-propylene (upper) and 3,3,3-D3-propylene (lower). Mass-to-charge (*m*/*z*) ratios of the products are also given.

electron density at the α-carbon atom, the radical center likely attacks the $=CH_2$ unit of the propylene molecule forming a doublet radical intermediate **i1** (Figures 5 and 6). A similar direction of an addition of an electrophilic reactant to double and triple bonds dictated the reaction dynamics of the bimolecular reactions of methylacetylene with CN radicals,[33] C_2D radicals,[34] $C(^3P_j)$,[35] and phenyl radicals.[17] Our best fits suggested the existence of a threshold energy to the reaction of 5−30 kJ mol^{-1}. This data agree well with the computed barrier to addition of 4−12 kJ mol^{-1}.[20] The addition process to the α-carbon atom of propylene leads to a weakly stabilized reaction intermediate **i1** and accounts for the indirect scattering dynamics as observed experimentally. This intermediate can emit a hydrogen atom from the α-carbon atom forming the *cis*/*trans*-1-phenylpropylene (*cis*/*trans*-$CH_3CHCHC_6H_5$) product (**p1**/**p2**) via a loose exit transition state located only 8 kJ mol^{-1} above the separated products. Recall that this loose exit transition state was predicted on the basis of the center-of-mass translational energy distribution. Note that our experiments are not sensitive enough to predict a branching ratio for the *trans*- versus *cis*-1-phenylpropylene (*cis*-$CH_3CHCHC_6H_5$) isomers.

Additionally, we should keep in mind that the crossed beam reaction of phenyl radicals with 3,3,3-D3-propylene (CD_3-$CHCH_2$) indicates that the emitted hydrogen atom originates from the vinyl group. Here an attack of phenyl on the α-position followed by a hydrogen loss from the $=CH_2$ unit can account for the observed ions in the TOF spectra, the loose exit transition state, and the energetics of the reaction (Figure 6). On the other hand, the attack of the phenyl radical at the β-carbon atom would lead to a D3-intermediate $C_6H_5CD_3CHCH_2$ that can also emit a hydrogen atom forming $C_6H_5CD_3CCH_2$ (**p3**). However, the exit transition state of this pathway is rather tight (21 kJ mol^{-1} above the separated products), and the overall reaction is endoergic by about 9 kJ mol^{-1}.[20] Therefore, a comparison of these data with the experimental results and the fact that the attack on the β-position is not favorable (see above) suggest that this reaction pathway is less dominant than an addition of the phenyl radical to the $=CH_2$ unit followed by an atomic hydrogen loss from the latter.

Finally, we would like to discuss the laboratory data obtained from the reaction of phenyl radicals with 1,1,2-D3-propylene (CH_3CDCD_2). To explain the experimentally observed atomic hydrogen loss, we have to suggest an addition of the phenyl radical to the $=CD_2$ unit; this leads to the formation of a D3-intermediate $CH_3CDCD_2C_6H_5$ (Figure 6). The latter can emit a hydrogen atom leading to the D3−**p3** product through a tight exit transition state, i.e., D3-3-phenylpropene ($H_2CCDCD_2C_6H_5$). Since the reactions with partially deuterated D3-propylene molecules assisted to identify two distinct hydrogen elimination pathways, we attempt now to estimate the branching ratios of the formation of **p1/p2** versus **p3**. It should be stressed that, to derive accurate branching ratios, it is necessary to collect the fragmentation ions arising from dissociative ionization of the parents in the electron impact ionizer. Also, it is important to have a laboratory angular distribution of both reaction channels available.[36] However, in cases of isotopically labeled experiments, we have shown that, if the laboratory angular distributions have a similar pattern, i.e., for reaction channels that have comparable available energies, it is feasible to utilize the TOF spectra recorded at the center-of-mass angles for the parent ions to estimate the branching ratios. This has been conducted successfully for the reactions of cyano radicals (CN)[33] and D1-ethynyl (CCD)[34] with D3-methylacetylene (CD_3CCH) to accuracy within 10%. Therefore, we can attempt to estimate the branching ratios of the channels based on the signal at m/z = 121 for the reaction of phenyl radicals with the 3,3,3-D3-propylene and 1,1,2-D3-propylene reactants at the corresponding center of mass angles (Figure 3). If we apply this procedure, our experimental data propose a branching ratio of the partially deuterated **p1/p2** versus **p3** products of 5.7 ± 2.1, i.e., about 80−90% of *cis*/*trans* D3-1-phenylpropene ($CD_3CHCHC_6H_5$) and 10−20% of D3-3-phenylpropene ($H_2CCDCD_2C_6H_5$). This order of magnitude agrees very well with the energetics of the reactions and the enhanced production of the thermodynamically more stable product molecule.

4.3. Comparison with the Phenyl−Methylacetylene Reaction. It is interesting to compare the chemical dynamics of the phenyl−propylene system with those of the phenyl−methylacetylene reaction investigated earlier in our group.[17] Utilizing D3-methylacetylene, the authors found that, at similar collision energies, the phenyl radical adds to the α-carbon atom of the methylacetylene molecule, leading to a $CD_3CCHC_6H_5$ intermediate. Similar to the phenyl−propylene system, the attack

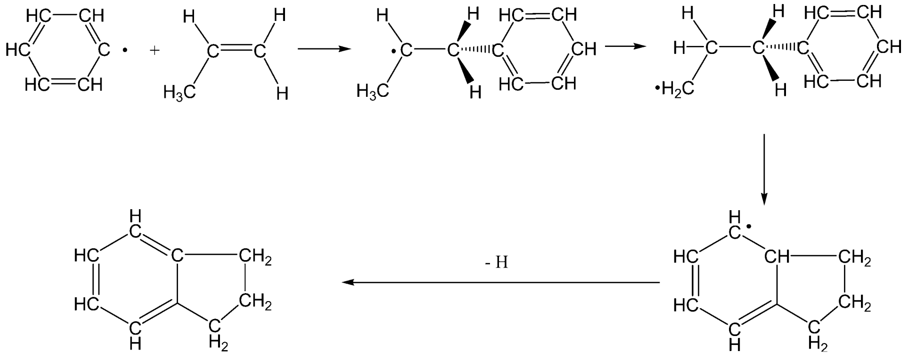

Figure 7. Proposed reaction sequence to form indane in low-temperature hydrocarbon flames from reaction of phenyl radicals with propylene.

to the least substituted carbon atom is directed by the screening effect of the methyl group and by the enhanced electron density of the α-carbon atom. For both reactions, the intermediates were short-lived, as evident from the forward-peaked center-of-mass angular distributions. However, for the phenyl−methylacetylene system, we observed a ratio at the poles, $I(180°)/I(0°)$, of 0.17 ± 0.05 versus 0.5 ± 0.1 for the phenyl−propylene system. The previous analysis of the reaction of phenyl radicals with methylacetylene suggested a lifetime of the reaction intermediate of less than 0.3 ps. However, utilizing the osculation complex model and the rotational constants of the $CH_3CHCH_2C_6H_5$ of the phenyl−propylene reaction ($I_A = 2.4 \times 10^{-45}$ kg m^2, $I_B = 7.7 \times 10^{-45}$ kg m^2, $I_C = 8.9 \times 10^{-45}$ kg m^2), we can estimate the lifetime of the reaction intermediate **i1** rotating around its *A*, *B*, or *C*-axis to be about 0.6, 1.3, and 1.5 ps. Therefore, this simple consideration implies that the lifetime of the $CH_3CCHC_6H_5$ reaction intermediate formed in the phenyl−methylacetylene reaction is less than the lifetime of the $CH_3CHCH_2C_6H_5$ complex accessed in the reaction of phenyl radicals with propylene. It should be noted that, in case of the $CH_3CCHC_6H_5$ intermediate (methylacetylene reaction), the authors only observed the emission of a hydrogen from the acetylenic carbon atom leading to the formation of $CH_3CCC_6H_5$, whereas in the current experiments (propylene), the $CH_3CHCH_2C_6H_5$ intermediate was also found to decompose predominantly via emission of the hydrogen atom connected to the α-carbon atom, but in addition, a minor pathway was verified to be the ejection of atomic hydrogen from the γ-carbon atom (the methyl group). The authors deduced that the lifetime of the $CH_3CCHC_6H_5$ intermediate (methylacetylene reaction) was too short to allow an energy “flow” from the position of the initial carbon−carbon single bond formation to the terminal carbon−hydrogen bond; as verified experimentally, this hindered the formation of the 1-phenylallene isomer ($C_6H_5HCCCH_2$) and only supports the synthesis of $CH_3CCC_6H_5$. However, in case of the propylene reaction, the observation of both *cis*/*trans*-1-phenylpropene ($CH_3CHCHC_6H_5$) and 3-phenylpropene ($H_2CCHCH_2C_6H_5$) could suggest that the energy randomization is more complete and that energy could flow from the activated carbon−carbon single bond to the methyl group in the $CH_3CHCH_2C_6H_5$ complex to allow a carbon−carbon bond rupture and hence also the formation of 3-phenylpropene ($H_2CCHCH_2C_6H_5$). This could be the result of the additional hydrogen atoms in the propylene molecule which increase the number of vibration modes by six in the phenyl−propylene system.

5. Conclusions and Summary

In our laboratory, we have investigated the reactions between phenyl radicals (C_6H_5) and propylene (CH_3CHCH_2) together with its D6- and D3-isotopologues under single collision conditions utilizing a crossed molecular beams machine. The chemical dynamics extracted from the data propose indirect (complex forming) dynamics that are initiated by an addition of the phenyl radical to the α-carbon atom (C1 carbon atom) of the propylene molecule at the $=CH_2$ unit. This leads to the formation of a radical intermediate ($CH_3CHCH_2C_6H_5$) on the doublet surface. Investigations with D6-propylene suggested that only a deuterium atom is emitted; the phenyl group was found to stay intact. Studies with 1,1,2-D3- and 3,3,3-D3-propylene indicated that the initial collision complexes $CH_3CDCD_2C_6H_5$ (from 1,1,2-D3 propylene) and $CD_3CHCH_2C_6H_5$ (from 3,3,3-D3 propylene) eject both a hydrogen atom via loose exit transition states to form the D3-isotopomers of 3-phenylpropene ($H_2CCHCH_2C_6H_5$) (10−20%) and *cis*/*trans*-1-phenylpropene ($CH_3CHCHC_6H_5$) (80−90%), respectively. Despite the enhanced lifetime of the reaction intermediate compared to the related phenyl−methylacetylene system studied earlier in our laboratory, the lifetime of the reaction intermediate is still too low—at least under our experimental conditions—to allow the formation of the indane molecule (Figure 7). At lower collision energies and hence corresponding lower temperatures in combustion flames, a possible reaction scenario, which still remains to be confirmed experimentally and/or computationally, is that the enhanced lifetime of the addition complex could support a hydrogen shift from the γ to the β carbon atom followed by ring closure and emission of a hydrogen atom from the benzene ring. Recall that, at our high collision energy, the reaction of phenyl radicals with D6-propylene and the sole observation of the atomic deuterium channel clearly indicated that indane was not a reaction product. However, lower collision energies might trigger the formation of indane, as proposed in Figure 7.

Acknowledgment. This work was supported by the US Department of Energy, Basic Energy Sciences (DE-FG02-03ER15411). We would also like to thank Ed Kawamura (University of Hawaii, Department of Chemistry) for assistance.

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