Forming Benzene in Flames by Chemically Activated Isomerization

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Benzene is not formed in flames by high-pressure-limit addition reactions, as had been implied previously, but by chemically activated addition and isomerization reactions. Possible mechanisms were tested by comparing predicted benzene formation rates (from measured reactant concentrations and predicted rate constants) against measured net formation rates of benzene. First, mole-fraction and rate data for molecules and free radicals were measured in a lightly sooting, laminar, premixed flame of C₂H₂/O₂/Ar at 1000-1700 K and 2.67 kPa (20 Torr) by using molecular-beam mass spectrometry. Second, mechanisms were screened in this flame and a similar 1,3-butadiene flame by using high-pressure-limit rate constants. Third, pressure-dependent rate constants for all channels of successful mechanisms were analyzed by bimolecular quantum-RRK calculations. Finally, data tests with these more accurate rate constants showed that only additions of vinylic $1-C_4H_5$ and $1-C_4H_5$ radicals to C_2H_2 were fast enough to account for the highest observed rates of benzene formation, forming benzene and phenyl "directly" by chemically activated channels. These reactants have been suggested before, but the pathways are crucially different from high-pressure-limit routes. A similar addition of C_2H_3 to C_4H_6 also contributed in the butadiene flame at lower temperatures.

Introduction

Benzene is formed from smaller, nonaromatic hydrocarbons in flames and in cracking processes, but its formation mechanism has remained elusive. For combustion, this question is especially significant because polycyclic aromatic hydrocarbons and soot, which are undesirable pollutants, probably grow from single aromatic rings. Benzene may be the crucial, first single-ring aromatic, or it may be a telltale byproduct of the process.

Many mechanisms have been suggested, but few have been tested. In all cases, energy-transfer effects like falloff have been ignored.

However, aromatics grow from smaller hydrocarbons by association reactions, in which energy-transfer effects can be quite important. When reactants R and R' combine, ground-state A is not formed directly. Instead, higher-energy forms, A*, are first formed. Excess energy above the ground state comes not only from thermal energy of the reactants but also, significantly, from the higher chemical energy of the newly formed species relative to ground-state A. These "chemically activated" A* can be stabilized by energy-removing collisions to form A (classical addition or addition/stabilization). If stabilization is too slow-i.e., if total concentration [M] = P/RT is too low—then A* molecules may revert to reactants without observable net reaction-classical falloff. They also may unimolecularly decompose to new products (chemically activated addition/decomposition) or isomerize to I* without forming ground-state A. Newly formed I* are also chemically activated relative to ground-state I. They may revert to A*, be stabilized (isomerization/stabilization), or decompose (isomerization/decomposition). Usually, A* and I* are not observable, so each of the thermal products will correspond to a different rate constant, here written as $k_{a/s}$, $k_{a/d}$, $k_{i/s}$, and $k_{i/d}$ based on apparent bimolecular reaction of the thermal reactants.

Chemically activated isomerization is a key to explaining benzene formation, identified here by testing a broad range of mechanisms against benzene formation rates in two flames. This result is fundamentally different from previous thinking because the effects of chemical activation (1) impede formation of the previously assumed thermalized intermediates but (2) avert their oxidation while (3) opening new, more effective channels. Thermalized intermediates can be attacked and destroyed by bimolecular reactions, while chemically activated intermediates can form aromatic rings faster than bimolecular collisions, stabilizing or reactive, can take place. In effect, aromatics are formed "directly" from the reactants without observable intermediates.

Previous Tests. Quantitative tests of benzene formation mechanisms against data have been published only by Cole et al., by Frenklach and co-workers,^{2,3} by Colket,⁴ and by Harris et al.⁵ The present study was provoked by the question of whether falloff affected conclusions of such studies.

Cole et al.¹ proposed a 1-C₄H₅ (*=-= or 1,3-butadienyl)⁶ + C_2H_2 pathway

$$===++==+=-=+ (R1)$$

$$=-=-=$$
 \rightarrow cyclohexadienyl (R2)

cyclohexadienyl \rightarrow benzene + H (R3)

on the basis of tests in a low-pressure (2.67 kPa or 20 Torr), $C_4H_6/O_2/Ar$ flat flame. Mole fractions of stable and free-radical species were measured by using molecular-beam mass spectrometry (MBMS). For selected pathways to benzene, rate constants were estimated by analogy or transition-state theory, and rates were predicted by using these rate constants, the mole fractions, and pseudo-steady-state assumptions. When predicted and measured rates of benzene formation were compared, the only satisfactory pathway was R1-3. The addition reaction was assumed to be rate-limiting, and its rate constant was estimated to be $10^{11.2} \exp(-(3.7 \text{ kcal/mol})/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ by thermochemical kinetics.

Frenklach and co-workers proposed and tested a $1-C_4H_3$ (*=== or 1-buten-3-ynyl) + C_2H_2 pathway, also with apparent success. For shock-tube pyrolyses of C_2H_2 at 1700–2300 K and 500–700 kPa (5-7 atm),² they concluded that

$$\equiv -= + \equiv \rightarrow \equiv -= -= -$$
 (R4)

$$\equiv - = - \Rightarrow phenyl$$
(R5)

was the major route to the first aromatic ring. This pathway was inferred from a 600-reaction, 180-species model by comparing

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^{=&}quot;. ----", and subsequent species to follow is (6) Typography for \equiv meant to be suggestive rather than precisely descriptive of structures; e.g., H atoms are omitted and carbon skeletons may in fact be bent.

several pathways within the model using ultimate production of soot (measured by light absorption) as an experimental test. The predicted maximum yield of soot was lower by a factor of 4 than the measured maximum, and temperatures of soot generation were shifted (predicted 1450–1800 K vs measured 1730–2250 K); however, a bell-shaped temperature dependence was correctly predicted. Compared to other pathways in the analysis, the 1-C₄H₃ route was faster by orders of magnitude. More recently, Frenklach and Warnatz³ compared predictions to stable-species data from low-pressure acetylene flames, finding semiquantitative agreement. Pathways involving R4,5 and R1 followed by an overall R2+3 were predicted to be important.

Colket measured and modeled concentrations of stable species from C_2H_2 and vinylacetylene (3-butenyne) pyrolyses in a single-pulse shock tube at 800 kPa of Ar.⁴ Three routes to aromatic rings were considered: (1) pathway 1–3 (written as an overall reaction with addition assumed to be rate-limiting, as it had been in the study of Cole et al.,¹ but with the use of a different rate constant from Weissmann and Benson⁷); (2) pathway R4,5 (written as separate reactions); and (3) $C_2H_3 + C_4H_4$ (written as an overall reaction to form benzene + H). After fitting rate constants for reactions 4 and 5 and $C_2H_3 + C_4H_4$ within a 56reaction mechanism, Colket concluded that R1–3 was most important for C_2H_2 pyrolysis below 1500 K; $C_2H_3 + C_4H_4$ was dominant in C_4H_4 pyrolysis below 1600 K; and R4,5 dominated in C_2H_2 pyrolysis above 1500 K and in C_4H_4 pyrolysis above 1600 K.

Finally, Harris et al.⁵ measured concentrations of stable single-ring aromatics in atmospheric pressure, $C_2H_4/O_2/Ar$ flat flames and modeled the flame chemistry. They wrote pathway R1-3 as an overall reaction using the rate constant of Cole et al.,¹ and an overall rate constant for pathway R4,5 was fitted to the data. For the 193-reaction mechanism, sensitivity analysis indicated that R1-3 contributed slightly overall, dominating below 1000 K, but that R4,5 dominated in the 1450–1600 K region of maximum benzene production.

Falloff was not considered in these or any other previous hypotheses. Rate constants have either been predicted by thermochemical kinetics, which gives only high-pressure-limit rate constants, or fitted within a mechanism.

Implications of Correcting the High-Pressure-Limit Assumption. Falloff can be significant at flame temperatures, as recognized for unimolecular decompositions,⁸ but chemical activation in bimolecular reactions can open "new" channels precisely because the conditions for addition/stabilization are unfavorable.

When an adduct is initially formed, it contains energy released by chemical bond formation plus thermal energy from the reactants. Excess energy relative to the thermalized, ground state must be dissipated by energy-removing collisions if the adduct is to be stabilized. If stabilization is too slow and if it has no alternatives, the energized adduct will decompose to the reactants, making the effective rate of addition/stabilization slower than the highpressure limit.

Significantly for benzene formation, the energized adduct also may decompose or isomerize unimolecularly to new products. Such pathways are described as chemically activated because they are driven largely by the excess chemical energy released in the addition. This higher energy than in the thermalized adduct drives the unimolecular reaction rate of the energized adduct at a faster rate than the unimolecular rate of the thermalized adduct.

As a clarifying example, consider an energy diagram for the addition of $1-C_4H_5$ to C_2H_2 (Figure 1). Initially, the association reaction forms a chemically activated 1,3,5-hexatrienyl or $n-C_6H_7^*$. This energized adduct may be collisionally stabilized to thermal $n-C_6H_7$, it may decompose to reactants, it may decompose to 3,5-hexadien-7-yne plus H, or it may isomerize. Total energy is conserved in isomerization, so the species formed is a hot cyclohexadienyl, $c-C_6H_7^*$, with the same energy content as the initial



Figure 1. Energy diagram for product channels of $1-C_4H_5 + C_2H_2$ association.

adduct but with much more excess energy relative to its ground state. The chemically activated cyclohexadienyl can itself isomerize, it can be collisionally stabilized, or it can decompose to benzene and H. Thus, four different reaction channels could be observed for the association reaction, as shown in R1, R6, R7, and R8:

addition/stabilization:

$$1-C_4H_5 + C_2H_2 \rightarrow n-C_6H_7^* \rightarrow n-C_6H_7 \qquad (R1)$$

addition/decomposition:

$$1 - C_4 H_5 + C_2 H_2 \rightarrow n - C_6 H_7^* \rightarrow = = + H$$
 (R6)

isomerization/stabilization:

$$1-C_4H_5 + C_2H_2 \rightarrow n-C_6H_7^* \rightarrow c-C_6H_7^* \rightarrow c-C_6H_7 \qquad (R7)$$

isomerization/decomposition:

$$1-C_4H_5 + C_2H_2 \rightarrow n-C_6H_7^* \rightarrow c-C_6H_7^* \rightarrow benzene + H$$
(R8)

Their respective rate constants $k_{a/s}$, $k_{a/d}$, $k_{i/s}$, and $k_{i/d}$ are determined by competitions among collisional stabilization and unimolecular reactions of the chemically activated intermediates.

Note that the falloff ratio k/k_{∞} must be the same for $n-C_6H_7 \rightarrow 1-C_4H_5 + C_2H_2$ or its reverse (R1), but analyzing falloff from unimolecular reaction theory will be incorrect if only the $n-C_6H_7 \rightarrow 1-C_4H_5 + C_2H_2$ product channel is considered. Calculations will be correct only if all the channels of $n-C_6H_7$ decomposition and isomerization are included.

More subtly, any conditions that implied the high-pressure limit for radical additions might instead permit the adduct to be destroyed by bimolecular reaction. Such conditions actually imply that collision rates with M are faster than any unimolecular reaction of the chemically activated $n-C_6H_7^*$ or $c-C_6H_7^*$. If M and the thermal species A can react, then A* may also react instead of losing energy by elastic collision, and no A would be produced.

Experimental Methods

The low-pressure flat-flame burner and molecular-beam mass spectrometer (MBMS) have been described previously.^{9,10} Feed gas was a mixture of 27.1% C_2H_2 , 67.9% O_2 , and 5.0% Ar, a fuel equivalence ratio of 2.40. Gas velocity from the burner was 0.50 m·s⁻¹ referenced to 298 K and 2.67 kPa.

Mole fractions of 38 species were measured as a function of distance from the burner by using molecular-beam sampling, beam modulation, and an in-line quadrupole mass spectrometer. For each species, ionizing electron energies were selected to yield only

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molecular ions. Species-vs-Ar signal ratio was related to concentration ratio by direct calibration for H_2 (estimated accuracy of $\pm 16\%$), CH₄ ($\pm 3\%$), C₂H₂ ($\pm 6\%$), CO ($\pm 3\%$), O₂ ($\pm 3\%$), Ar $(\pm 10\%)$, and CO₂ $(\pm 3\%)$; by O-atom balance in the postflame gas for H_2O (±25%); and by the method of relative ionization cross sections¹¹ for minor stable species and free radicals (accuracy within a factor of 2 except a factor of 3 for C_6H_5).

Temperature was measured with 1.2-mm-diameter Pt/Pt-13% Rh thermocouples coated with thin Y_2O_3 /BeO ceramic by the methods of Kent.¹² Low temperatures (to 1300 K) were measured directly by resistively heating the thermocouple to eliminate conduction to or from the gas; higher temperatures were determined from readings of the unheated thermocouple and the measured emissivity-diameter product. In the region of present interest, temperatures ranged from 500 to 1700 K with an uncertainty of ± 50 K. The temperature profile and mole-fraction profiles were aligned approximately by shifting the mole-fraction profiles toward the burner by two orifice diameters (1.10 mm).¹³ We took this correction to be acceptable beyond 2 mm (corrected units) from the burner.

Net reaction rates of formation were analyzed from the data for each species by using one-dimensional flow equations.¹⁴ The analysis involves axial differentiation of mole fraction to calculate diffusive flux of a species, which is summed with convective flux. Calculation of net formation rate is essentially a differentiation of the total flux with a flow-field correction.

The MBMS could distinguish isomers only if they had significantly different ionization potentials, so a sample from the flame was analyzed by GC/MS. Sample was withdrawn over a 4.00-h period through a microprobe positioned 5.0 mm above the burner. As the gases passed through a bed of XAD-2 polymer beads (a styrene-divinylbenzene copolymer), stable species were trapped for subsequent extraction by CH₂Cl₂ and analysis by GC/MS. A total of 174 stable species were measured and identified by molecular weight (68-180 range) or structure.^{10,15}

Experimental Data

Acetylene Flame. Data profiles for 0-6 mm from the burner are presented in Figure 2. Mole fraction points and smoothed curves are shown for benzene and the 11 species to be examined as possible reactants to benzene; temperature is also shown. Data points, fluxes, and reaction rates for all 38 species over 0-40 mm are tabulated elsewhere.¹⁰

Predicted and measured rates are compared here, so error analysis is important. First, experimental net rate of formation for benzene (or more correctly, for mass 78) is fast and positive in a region dominated by benzene diffusion. Thus at the position of fastest net production of benzene (2.9 mm), this rate is correct within a factor of 3, limited primarily by calibration uncertainty (factor of 2) and differentiation uncertainty (maximum factor of 2 occurs at about 2.9 mm). The ± 50 K precision for temperature causes only $\pm 3.7\%$ uncertainty in rate, primarily by its effect on gas density rather than on diffusivity. Second, rates are also calculated from predicted rate constants and measured reactant concentrations; again, uncertainties are dominated by calibration precisions, $\pm 6\%$ for C₂H₂ and a factor of 2 for the other species. Temperature effects are small, about $\pm 18\%$ for an activation energy of 20, $\pm 5\%$ for 10, and $\pm 6.6\%$ for zero kcal mol⁻¹.

The 78-amu species detected in the flame is primarily benzene, as shown by GC/MS. A usual test, measurement of the ionization potential, was not conclusive.¹⁰ The experimental ionization potential for mass 78 at 4.0 mm was 9.3 ± 0.5 eV, but the literature¹⁶ reports 9.25 eV for benzene, 9.50 for 3,5-hexadienyne,



Figure 2. Mole fractions of possible reactants in the benzene formation of a lightly sooting $C_2H_2/O_2/5\%$ Ar flame ($\phi = 2.40$): (a, top) H, Δ ; H_2 , ♦; CH_3 , ●; C_2H_2 , O; C_2H_4 , ♦; C_3H_3 , ▲; C_3H_4 , ∇ ; (b, bottom) C_2H_3 O; C₄H₃, \bullet ; C₄H₄, \bullet ; C₄H₅, \blacksquare ; C₄H₆, \diamond ; C₆H₆, \blacktriangle . Precision is ±50 K for temperature, $\pm 16\%$ for H₂, $\pm 6\%$ for C₂H₂, and a factor of 2 for all other species shown.

10.35 for 3-hexene-1,5-diyne. Other isomers containing CH₃ groups have ionization potentials varying from 9.20 to 10.35, and 5-methylenecyclopentadiene is at 8.36 eV. GC/MS analysis of mass 78 species was more successful, detecting benzene (72% of total mass 78 at this position) and three aliphatic C_6H_6 species. Ambiguities could not be resolved in this way for radical reactants and intermediates, which are destroyed in the microprobe.

Butadiene Flame. Mole fractions and estimated temperatures are reported by Cole et al.¹ from the same apparatus described above. They measured no mole fractions for CH_3 , C_2H_3 , or C_4H_3 , so analysis of reactions involving those species is not possible in their flame.

Analysis of Aromatics Formation in Test Flames

Approach. For a reaction to be part of a major pathway to benzene, its forward rate must be comparable to or greater than the measured (net) benzene formation rate. The following analyses apply this criterion by predicting the rate from measured concentrations of the radical and stable reactants, measured temperature, and predicted rate constants. An advantage of this approach is to uncouple the reaction in question from uncertainties about other reactions in the system. In contrast, predicting benzene formation from a "complete" trial mechanism is limited by prediction uncertainties in precursor concentrations.

Comprehensive Examination of Literature Hypotheses. In order to consider all possible routes to aromatic rings, literature hypotheses were gathered (Table I) and classified. For these

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TABLE I: Routes or Key Steps Suggested in the Literature for Aromatics Formation from Smaller Hydrocarbons, Listed Chronologically in Order of Suggestion

mechanism	ref
direct polymerization of C ₂ H ₂	17
CH ₂ and CH "fragments" incorporated into the formation of aromatics	18
Diels-Alder addition of 1,3-butadiene (C_4H_6) to ethylene (C_2H_3)	19, 20
alkene trimerization into rings	21
Diels-Alder addition of C.H. to cyclohexene	22
addition of 1.3-butadien-1-vl (1-C ₄ H ₄) to C ₂ H ₄ .	23
decomposition of the adduct to form 1.3.5-hexatriene	
(=-=-=), cyclization, and hydrogen loss	
$C_{2}H_{2}$ addition to $C_{4}H_{4}$. H-atom loss to form	7.23
1.3.5-hexatriene, cyclization, and hydrogen loss	,
combination of allyl radicals, hydrogen loss to form	23, 24
1,3,5-hexatriene, molecular cyclization, and hydrogen loss	,
addition of 1-buten-3-ynyl $(1-C_4H_3, *=-=)$ to C_2H_2 or	2, 25
other alkynes, followed by cyclization of the adduct to	
phenyl or its analogues	
Diels-Alder dimerization of C_4H_6 , eventually leading to	26
styrene	
dimerization of the C ₃ H ₃ species trimethine (*CH=CH-CH:	27
as opposed to the more stable 1,2-propadienyl)	
Diels-Alder addition of C_4H_6 (=-=) to C_2H_2 (=)	28
addition of 2-ethynyl-1-buten-3-ynyl ($=(-C_2H)-\equiv$) to	29
C_2H_2 , followed by adduct cyclization to ethynylphenyl	
radical	
addition of 1-C ₄ H ₅ (•=-=) to C ₂ H ₂ or other alkynes	1
(propyne, diacetylene, or vinylacetylene), cyclization of the	
adduct to a cyclohexadienyl structure, and H-atom	
elimination to form a stable aromatic	
sequence of additions and H abstractions by CH ₃ , β	29
scissions, and combinations of CH ₃ with resonantly	
stabilized radicals such as ally	
C_2H_3 addition to vinylacetylene, conversion of the C_6H_7	4
adduct to a cyclic C_6H_7 , and H-atom loss	21
addition and cyclization reactions of diradical $C_4H_2-C_4H_2$	31
uniters, leading to trietnynyl aromatics	27
forming a linear $C = u$ a cyclic $C = u$ and hence $u = u$	52
forming a linear $C_6 \Pi_7$, a cyclic $C_6 \Pi_7$, and belizene $\pm \Pi$	

routes, elementary steps either have been described or can be inferred. It then is useful to observe that the reactions involved can all be classified as being (1) molecular weight growth, (2) cyclization, or (3) hydrogen change by gain, loss, or shift.

Molecular weight growth is used here to mean increase in carbon number, for which radical additions, radical combinations, and Diels-Alder reactions have been proposed. Radical addition to a π bond has been proposed for various vinylic radicals including $C_{2}H_{3}$ itself,^{4,7,23} 1- $C_{4}H_{3}$,^{2,25} and 1- $C_{4}H_{5}$;^{1,23} additions of CH_{3}^{30} or $C_3H_3^{33}$ to π bonds also have been suggested. Combinations

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TABLE II: High-Pressure-Limit Rate Constants for Screening

association reacn	k_{∞} , cm ³ mol ⁻¹ s ⁻¹ , with <i>E</i> , kcal mol ⁻¹	source
radical additions		
$CH_3 + C_4H_6$	$8.1 \times 10^{10} \exp(-4.1/RT)$	а
$C_2H_3 + C_4H_4$	$3 \times 10^{11} \exp(-3/RT)$	b
$C_{2}H_{3} + C_{4}H_{6}$	$2.23 \times 10^{7} T^{1.31} \exp(-1.37/RT)$	С
$C_3H_3 + C_3H_4$	$3 \times 10^{11} \exp(-3/RT)$	b
$1 - C_4 H_3 + C_2 H_2$	$4.12 \times 10^{6} T^{1.646} \exp(-2.50/RT)$	с
$1 - C_4 H_5 + C_2 H_2$	$1.725 \times 10^{6} T^{1.792} \exp(-2.24/RT)$	с
$1 - C_4 H_5 + C_2 H_4$	$3 \times 10^{11} \exp(-3/RT)$	b
radical combinations	•••	
$C_3H_5 + C_3H_5$	8.5×10^{12}	d
$C_{3}H_{3} + C_{3}H_{3}$	8.5×10^{12}	е
$C_{2}H_{3} + C_{4}H_{5}$	1.7×10^{13}	f
Diels-Alder additions		
$C_4H_6 + C_2H_2$	$2.3 \times 10^{12} \exp(-35/RT)$	g
CH + CH	$2.3 \times 10^{10} \exp(-27/RT)$	ĥ

^aReference 34. ^bEstimate of Weissman and Benson (ref 7) for $C_{2}H_{3} + C_{4}H_{6}$; compare to estimate of 2.4 × 10¹¹ exp(-4/RT) by Cole (ref 35). 'This work, estimated by methods of thermochemical kinetics from $E_{\infty} = 3.5$ kcal mol⁻¹ at 400 K (ref 1) and from estimated ΔS^{*}_{298} and $\Delta C_p^*(T)$. ^d Used measurement by Van den Bergh and Callear (ref 36) at 298 K; Throssell (ref 37) has estimated 4×10^{12} cm³ mol⁻¹ s⁻¹ and Golden et al. (ref 38) measured 7.4 \times 10¹² at 913 K and 5.0 \times 1012 at 1063 K but noted that some falloff was a possibility. Based on $k(2C_3H_5 \rightarrow C_6H_{10})$. Based on $k(2C_3H_5 \rightarrow C_6H_{10})$ multiplied by 2 for nonidentical reactants. ^gEstimate of Cole et al. (ref 1). ^hUchiyama et al. (ref 39).



Figure 3. Screening comparisons for reactants that could form benzene in C₂H₂ flame: measured net rate of benzene formation, -=-; CH₃ + C_4H_6 , \triangleleft ; $C_2H_3 + C_4H_5$, \triangleright ; $C_2H_3 + C_4H_6$, \diamond ; $C_3H_3 + C_3H_3$, \times ; C_3H_3 + $C_{3}H_{4}$, Δ ; $C_{4}H_{3}$ + $C_{2}H_{2}$, ∇ ; $C_{4}H_{5}$ + $C_{2}H_{2}$, O; $C_{4}H_{5}$ + $C_{2}H_{4}$, *; $C_{4}H_{6}$ + C₂H₂, □.

of allyl radicals,^{23,24} trimethine-trimethine (CHCHCH),²⁷ and CH₃ with allyl and 2,4-pentadienyl³⁰ have been proposed to lead to benzene. Finally, Diels-Alder reactions produce both growth and cyclization. Conjugated diene structures like 1,3-butadiene may add concertedly across double bonds^{19,20,22,26} or triple bonds²⁸ to form cyclohexene or 1,4-cyclohexadiene structures, respectively.

Cyclizations that have been suggested include Diels-Alder cycloadditions and two isomerizations: molecular cyclization^{7,23,24} and radical self-addition^{1,2,25,29} (e.g., $\equiv -= -= - \rightarrow \text{ phenyl}$). Molecular cyclization, referring here to isomerization of 1,3,5hexatriene to 1,3-cyclohexadiene, 33 would proceed by a pericyclic pathway. In contrast, self-addition is another radical addition to a π bond, one which is the reverse of β -scission ring-opening of a cyclic radical.

Amounts and/or locations of H atoms change during the progress of most proposed mechanisms. For example, addition of either CH₃ or allyl to a π bond must leave an sp³ carbon from which H would have to be removed. Similarly, either C₂H or

TABLE III: Input Parameters for	r Calculations of Rate Cons	ants by Bimolecular Quan	ntum-RRK (mol, cm, s, kcal Units)
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	reactant sets				
	$1 - C_4 H_5 + C_2 H_2$	$1 - C_4 H_3 + C_2 H_2$	$C_2H_3 + 1,3-C_4H_6$	$1 - C_4 H_5 + C_2 H_3$	
a/s product a/d products i/s product i/d products no. 1 i/d products no. 2	$n-C_6H_7$ H + 1,3,5-cyclohexatriene c-C ₅ H ₇ H + benzene	$n-C_6H_5$ H + 3-hexene-1,5-diyne phenyl (c- C_6H_5) H + benzyne	$n-C_6H_9$ H + 1,3,5-hexatriene cyclohex-3-enyl H + 1,4-cyclohexadiene H + 1,3-cyclohexadiene	1,3,5-hexatriene H + 1,3,5-hexatrienyl 1,3-cyclohexadiene H ₂ + benzene	
$k_{s/s,\infty}$ (addition) $A_{m}E_{m}s^{-1}$, kcal/mol	$1.725 \times 10^{6} T^{1.792}$ exp(-2.24/RT) ^a	$4.12 \times 10^{6} T^{1.646}$ exp(-2.50/RT) ^a	$2.23 \times 10^7 T^{1.31} \exp(-1.37/RT)^a$	$8.5 \times 10^{12 b}$	
adduct to reactants adduct decompn isomerization reverse isomerization isomer decompn no. 1 isomer decompn no. 2	$2.63 \times 10^{14}, 43.7^{c}$ $4 \times 10^{12}, 36.7^{d,e}$ $1.7 \times 10^{11}, 7.0^{i}$ $1.0 \times 10^{14}, 53.2^{d}$ $2.0 \times 10^{13}, 26.0^{i}$	$2.83 \times 10^{14}, 43.3^{c} \\ 8 \times 10^{12}, 36.7^{d,f} \\ 4 \times 10^{10}, 7.0^{i} \\ 1.2 \times 10^{14}, 70.9^{d} \\ 4.9 \times 10^{13}, 87.5^{d,m}$	$\begin{array}{c} 1.27 \times 10^{13}, 47.3^{c} \\ 3 \times 10^{13}, 42.2^{d,g} \\ 2 \times 10^{11}, 8.0^{j} \\ 1.8 \times 10^{14}, 17.4^{d} \\ 4.7 \times 10^{13}, 37.4^{d,n} \\ 1.2 \times 10^{13}, 37.6^{d,o} \end{array}$	$8.0 \times 10^{16}, 114.4^{d}$ $1.9 \times 10^{14}, 110.0^{d,h}$ $7.8 \times 10^{11}, 29.9^{k}$ $2.85 \times 10^{15}, 43.9^{d}$ $3 \times 10^{13}, 62.0^{p}$	
E(isomer) - E(adduct) adduct $\langle \nu \rangle$, cm ^{-1 q} isomer $\langle \nu \rangle$, cm ^{-1 q} no. of oscillators	46.2 1050 1050 33	-63.9 990 1180 27	-9.4 990 1200 39	-14.0 1050 1110 36	

^aCalculated by thermochemical kinetics (see Table II). ^b From k_{∞} of allyl combination (see Table II). ^cCalculated by microscopic reversibility from Arrhenius tangent of addition rate constant at 1500 K. ^dCalculated by microscopic reversibility. ^eReverse (association) rate constant based on $k_{\infty}(H + C_4H_2) = 1.6 \times 10^{12} \exp(-1.0/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from ref 42, divided by reaction path degeneracy (RPD) of 4 sp carbon addition sites. ^fReverse rate constant based on $k_{\infty}(H + C_4H_2)/4$ multiplied by RPD = 2 for addition to 2- or 5-position of 3-hexene-1,5-diyne (=--==). ^gReverse rate constant based on $k_{\infty}(H + C_2H_4) = 1.6 \times 10^{12} \exp(-1.0/RT)$ from ref 42, divided by RPD of 2 sp² carbon addition sites and multiplied by RPD = 2 for addition to 2- or 5-position of 1,3,5-hexatriene (=-=-=). ^kAssociation rate constant of 1.6 × 10¹² (method of ref 43). ⁱA_m estimated by thermochemical kinetics, E_{w} as for radical addition (ref 44). ^jReference 7. ^kReference 33. ⁱBased on ref 45 and 46 at 550 K (average). "Reverse rate constant based on $k_{\infty}(H + \text{propyne}) = 6.5 \times 10^{12} \exp(-2.0/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref 42). "Based on k_{∞} for H + 2-butene (ref 34) corrected by thermochemical kinetics." Based on ref 40. "Based on k_{∞} for cyclohexene \rightarrow 1,3-cyclohexadiene + H₂ (ref 33). "Geometric mean of estimated frequencies.

vinylic additions to the end of a substituted acetylene would create an internal hydrogen-deficient site (e.g., $C_2H_3 + C_4H_4$ or = + implied are bimolecular abstraction of H, unimolecular elimination of H from cyclic radicals, unimolecular elimination of H₂ (most easily from 1,4-cyclohexadiene), and H-shift isomerization.

Each step must be fast enough, so the molecular-weight-growth steps were evaluated, initially at their high-pressure limits. All association steps that have been suggested were tested, and two radical combinations were added, $C_2H_3 + 1-C_4H_3$ and $C_2H_3 +$ $1-C_4H_5$. Falloff, cyclization, and H shifts then are further constraints.

Screening Using the High-Pressure Limit. To screen mechanisms before more detailed calculations were made, rates for the molecular-weight-growth steps were calculated from high-pressure-limit rate constants $k_{a/s,\infty}$ and the measured concentrations of possible reactants. This test is appropriately general, because $k_{a/s,\infty}$ is greater than or equal to the sum of rate constants for all individual channels. Thus, neither a thermal reaction sequence nor a chemically activated pathway can be faster than this high-pressure-limit rate. Reactants and $k_{a/s,\infty}$ for each test are presented in Table II.

For the acetylene flame, screenings at the high-pressure limit are presented in Figure 3. Only additions of $1-C_4H_3$ and $1-C_4H_5$ to C_2H_2 and combination $C_3H_3 + C_3H_3$ would be faster than the measured net benzene formation rate. Next fastest are C_3H_3 + C_3H_4 and $C_2H_3 + C_4H_5$, which would be slower than the measured rate but within factors of 6 and 10; these channels are within the

(35) Cole, J. A. A Molecular-Beam Mass-Spectrometric Study of Stoi-chiometric and Fuel-Rich 1,3-Butadiene Flames. M.S. Thesis, Department of Chemical Engineering, Massachusetts Institute of Technology, 1982.

(36) Van den Bergh, H. E.; Callear, A. B. Trans. Faraday Soc. 1970, 66, 2681.

feasibility limits because measured rate and predicted rate each have precisions of a factor of 4. Screened rates for Diels-Alder reactions and radical additions to C_2H_4 , C_4H_4 , and C_4H_6 were even slower, 2 or more orders of magnitude smaller than the measured rate even in this limit.

For the butadiene flame (Figure 4), screening implies that $1-C_4H_5 + C_2H_2$ and $C_2H_3 + 1,3-C_4H_6$ were the most feasible association reactions in the high-pressure limit. $C_2H_3 + C_4H_5$ was a factor of 10 slower than the measured rate and so was marginally feasible. The fastest infeasible alternative was C₃H₃ + C_3H_3 , a constant factor of 20 too slow up to 8 mm, where destruction of benzene begins to force the measured net rate toward negative values. While $1-C_4H_3 + C_2H_2$ might contribute, it was not tested because no C_4H_3 data were reported for this flame. Although C_2H_3 , C_3H_3 , C_3H_4 , and C_4H_6 were measured, rates for $C_2H_3 + C_4H_6$ and $C_3H_3 + C_3H_4$ were too slow.

To summarize the two screenings, only six sets of reactants were feasible in the high-pressure limit: (1) $1-C_4H_5/C_2H_2$, feasible in both flames; (2) $1-C_4H_3/C_2H_2$, tested only in the acetylene flame; (3) $C_2H_3/1$, 3- C_4H_6 , feasible only in the butadiene flame; (4) C_2H_3/C_4H_5 , marginally feasible in the butadiene flame, marginally infeasible in the acetylene flame; (5) C_3H_3/C_3H_3 , feasible only in the acetylene flame; and (6) C_3H_3/C_3H_4 , feasible only in the acetylene flame.

Although $C_3H_3 + C_3H_3$ and $C_3H_3 + C_3H_4$ seem promising, subsequent cyclization and hydrogen redistribution are serious difficulties. Hurd et al.²⁷ suggested that $C_3H_3 + C_3H_3$ might proceed by isomerization from the ground-state propargyl (C-H₂CCH) to trimethine (CHCHCH). Actually, this change should require about 70 kcal/mol, making equilibrium trimethine concentrations much lower than those of propargyl. Alternatively, if propargyl were to combine, it does not appear that the resulting C_6 species could easily form an aromatic ring. Ground-state C_3H_3 has two resonance structures, 2-propynyl (HC=C-CH₂ \cdot or = $-CH_2^{\bullet}$) and propadienyl ($^{\bullet}CH=C=CH_2$ or $^{\bullet}==$), so simple combinations would form \equiv -CH₂-CH₂- \equiv , \equiv -CH₂- \equiv , and ==== isomers. The problems of H shifts were considered sufficient to rule out $C_3H_3 + C_3H_3$ for now and, by similar considerations, $C_3H_3 + C_3H_4$.

Detailed Calculations of Rate Constants. Rate constants were calculated at 2.67 kPa (20 Torr) for all channels of the chemically

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TABLE IV: Expressions for Channel-Specific, Bimolecular Rate Constants with Pressure Effects Included, Calculated by Bimolecular Quantum-RRK and Fitted over 400-1600 K to $A'T^b \exp(-E'/RT)$ with A' in cm³ mol⁻¹ s⁻¹ and E' in kcal mol⁻¹

	at 2.6	at 2.67 kPa of CO			at 101 kPa of N_2		
reacn	A'	Ь	<i>E'</i>		Ь	<u> </u>	
$1-C_4H_5 + C_5H_2$	· · · · · · · · · · · · · · · · · · ·				*********		
$\rightarrow n-C_6H_7$	8.74×10^{12}	-1.27	3.56	7.24×10^{14}	-1.38	3.98	
$\rightarrow n - C_6 H_6 + H$	1.17×10^{-15}	7.84	2.04	3.47×10^{-15}	7.73	2.50	
$\rightarrow c-C_6H_7$	1.96×10^{19}	-3.35	5.24	7.12×10^{21}	-3.64	6.26	
→ benzene + H	1.90×10^{7}	1.47	4.91	2.38×10^{8}	1.18	3.74	
$1-C_4H_3 + C_2H_3$							
$\rightarrow n - C_6 H_5$	1.73×10^{11}	-0.41	4.03	6.17×10^{15}	-1.51	4.83	
$\rightarrow n - C_6 H_4 + H$	29.6	3.33	9.62	2.77×10^{-7}	5.59	6.02	
→ phenyl	3.33×10^{24}	-3.89	9.21	7.00×10^{14}	0.86	6.37	
→ benzyne + H	1.64×10^{9}	0.73	12.18	3.00×10^{-11}	6.48	6.64	
$C_2H_3 + 1,3-C_4H_6$							
$\rightarrow n - C_6 H_9$	5.48×10^{28}	-5.31	9.32	1.48×10^{12}	-0.17	3.24	
\rightarrow 1,3,5-C ₆ H ₈ + H	1.00×10^{10}	1.05	14.01	5.48×10^{-15}	8.20	6.29	
$\rightarrow c-C_6H_9$	1.64×10^{29}	-6.12	9.63	7.06×10^{13}	-1.35	3.99	
→ cyclohexadiene + H	2.28×10^{12}	-0.24	9.92	4.15×10^{-11}	6.39	2.44	
$C_2H_3 + 1-C_4H_5$							
\rightarrow 1,3,5-C ₆ H ₈	2.90×10^{15}	-0.78	0.98	1.50×10^{13}	-0.075	0.10	
\rightarrow 1,3,5-C ₆ H ₇ + H	8.28×10^{-28}	11.89	5.04	3.55×10^{-43}	16.16	-0.17	
→ 1,3-cyclohexadiene	5.50×10^{15}	-1.67	1.47	8.53×10^{13}	-1.11	0.82	
→ benzene + H,	2.80×10^{-7}	5.63	-1.89	1.84×10^{-13}	7.07	-3.61	



Figure 4. Screening comparisons for reactants that could form benzene in 1,3-butadiene flame: measured net rate of benzene formation, :; C2H3 + C_4H_4 , +; C_2H_3 + C_4H_5 , >; C_2H_3 + C_4H_6 , \diamond ; C_3H_3 + C_3H_3 , X; C_3H_3 + C_3H_4 , Δ ; C_4H_5 + C_2H_2 , O; C_4H_5 + C_2H_4 , *; C_4H_6 + C_2H_2 , \Box ; C_4H_6 + C₂H₄, ⊒.

activated associations $1-C_4H_5 + C_2H_2$, $1-C_4H_3 + C_2H_2$, $C_2H_3 + C_2H_3 +$ 1,3-C₄H₆, and C₂H₃ + 1-C₄H₅ by using bimolecular quantum-RRK, an update and adaptation by Dean⁴⁰ of the quantized unimolecular reaction theory of Kassel.⁴¹ Accuracies of quantum-RRK or RRKM calculations should be comparable in cases such as those here, each method limited by the same input uncertainties in A_{∞} and E_{∞} . To approximate weak-collision effects, a first-order rate constant for collisional stabilization $\beta Z_{LJ}[M]$ is used in the adaptation, where β is an approximate collision efficiency and Z_{LL} is a Lennard-Jones collision frequency rate constant. Uncertainties due to the estimation of β are assessed below in the Discussion section by a simple analysis of state-to-state energy transfer.

Table III contains the needed input parameters for bimolecular quantum-RRK calculations: k_{∞} 's, number of oscillators, geo-



Figure 5. Rate constants predicted for product channels of $1-C_4H_5$ + C_2H_2 at 2.67 kPa (20 Torr), M = CO.

metric-mean frequencies, and isomer-adduct energy difference. The other inputs needed are collisional properties of the adduct, the isomer, and the third-body gas. The reasonable assumption was made that for all C_6 adduct and isomer species, the Lennard-Jones parameters for benzene could be used: $\sigma = 5.349$ Å and $\epsilon/\kappa = 412.3$ K.⁴⁷ CO was the predominant species in these flames and was used as the third-body gas M for the 2.67-kPa calculations. Using other light gases did not change the result significantly. A value of $-\langle \Delta E_{coll} \rangle = 1200 \text{ cal/mol}$, the average amount of energy transferred per mole of collisions with CO, was selected from a review of literature data.¹⁰ Lennard-Jones parameters for CO were $\sigma = 3.65$ Å and $\epsilon/\kappa = 98.1$ K.⁴⁸

Calculated rate constants were fitted to semi-Arrhenius equations from 400 to 1600 K. These fits are listed in Table IV.

(i) Formation of Benzene from $1-C_4H_5 + C_2H_2$. "Direct" formation of benzene is predicted to dominate the product channels of $1-C_4H_5 + C_2H_2$ at 2.67 kPa for all temperatures (Figure 5), and, furthermore, its rate constant $k_{i/d}$ is nearly equal to $k_{a/s,\infty}$. The chemically activated adduct goes primarily to $c-C_6H_7$ * be-

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Figure 6. Rate constants predicted for product channels of $1-C_4H_3 + C_2H_2$ at 2.67 kPa (20 Torr), M = CO.

cause of (1) excess energy in n-C₆H₇* relative to the low barrier to cyclization, required to offset loss of entropy, and (2) difficulty of collisional stabilization. Likewise, the higher excess of energy in c-C₆H₇* and a low exit barrier favor β scission of c-C₆H₇* (forming benzene) over collisional stabilization or reisomerization.

At this pressure, $k_{i/d}$ drops slightly below $k_{a/s,\infty}$ only above 1400 K. This drop is not caused by diversion into other product channels but rather by the growing importance of the decomposition back to reactants, $n-C_6H_7^* \rightarrow 1-C_4H_5 + C_2H_2$. Decomposition of $n-C_6H_7^*$ to $H + n-C_6H_6$ is the next most important product channel, but $k_{a/d}$ is an order of magnitude slower than $k_{i/d}$ even at 2000 K. Both stabilization channels (to $n-C_6H_7$ and $c-C_6H_7$) are 2 or more orders of magnitude slower than the primary channel at all temperatures.

(ii) Formation of Phenyl from $1-C_4H_3 + C_2H_2$. Chemically activated $n-C_6H_5^*$ is formed by addition of $1-C_4H_3$ and C_2H_2 , and just as for $n-C_6H_7^*$, it isomerizes rapidly to a chemically activated cyclic structure that has a much lower ground-state energy. Unlike $c-C_6H_7^*$, though, $c-C_6H_5^*$ (phenyl*) has a higher exit barrier for decomposition relative to that for reisomerization (87.5 vs 70.9) because, unlike benzene, benzyne ($c-C_6H_4$) is a highly strained, high-energy species. Thus, collisional stabilization of the cyclic intermediate to thermal phenyl is feasible.

Calculations at 2.67 kPa (Figure 6) confirm the importance of the phenyl channel, but they also show that this isomerization/stabilization channel is affected more by pressure and alternative channels than was $1-C_4H_5 + C_2H_2 \rightarrow H +$ benzene. The rate constant $k_{i/s}$ to phenyl has a maximum because collisional stabilization becomes more difficult as temperature increases; i.e., β and [M] decrease. High temperatures also extend the energy distribution of excited *n*-C₆H₅* and c-C₆H₅* states to higher energy levels, where chemically activated decomposition is more likely.

Thus, phenyl is still the dominant product up to 1650 K, but the rate constant has a maximum at 1150 K and declines sharply at higher temperatures. Above 1650 K, chemically activated addition/decomposition to $H + n-C_6H_4$ predominates. Contributions of thermalized addition and of isomerization/decomposition are minor, never exceeding 4 or 6% of the total rate constant, respectively.

(iii) Addition of C_2H_3 to Butadiene. The nascent adduct, chemically activated $n-C_6H_9^*$ ($=-CH_2-=-CH_2^{-*}$ or $=-CH_2-CH_2^{-*}$), could cyclize to a chemically activated cyclohexenyl and decompose to 1,3- or 1,4-cyclohexadiene by β scission. Instead, as shown in Figure 7, addition/stabilization to $n-C_6H_9$ and addition/decomposition to 1,3,5-hexatriene + H are predicted to dominate. Chemically activated isomerization is not important, in contrast to the previous cases, because the ground-state isomer c-C_6H_9 and adduct $n-C_6H_9$ have similar energies. The isomer is



Figure 7. Rate constants predicted for product channels of $C_2H_3 + C_4H_6$ at 2.67 kPa (20 Torr), M = CO.



Figure 8. Rate constants predicted for product channels of $1-C_4H_5 + C_2H_3$ at 2.67 kPa (20 Torr), M = CO.

only 9 kcal/mol more stable than the adduct, compared to 46 for $c-C_6H_7$ (which has more resonance stabilization) and 64 for phenyl (which has aromatic stabilization). This stabilization is insufficient to compensate for the loss of entropy in cyclization.

Test of Predicted Rates against Measurements. With rate constants that correctly allow for pressure and chemically activated channels, rates for the different channels can be predicted and compared to the measured net rates of benzene formation. The rate of benzene formation is predicted directly for $1-C_4H_5 + C_2H_2$. For reactions that form intermediates such as $1-C_4H_3 + C_2H_2 \rightarrow$ phenyl, applying this test assumes that benzene formation via





Figure 9. Test of product-specific rate constants that could lead to benzene in C_2H_2 flame: measured (net) rate, $-\blacksquare$, $C_4H_3 + C_2H_2 \rightarrow$ phenyl, ∇ ; $C_4H_5 + C_2H_2 \rightarrow$ benzene + H, O; $C_2H_3 + C_4H_5 \rightarrow 1,3,5$ - C_6H_8 , \triangleright ; sum of predicted k's, ---.

the intermediate can be no faster than the rate of formation for the intermediate.

The acetylene flame is tested in Figure 9. Only "direct" pathways involving the chemically activated isomerizations

$$1-C_{4}H_{5} + C_{2}H_{2} \rightarrow (===)^{*} \rightarrow (cyclohexadienyl)^{*} \rightarrow benzene + H (R8)$$
$$1-C_{4}H_{5} + C_{2}H_{2} \rightarrow (===)^{*} \rightarrow (cyclohexadienyl)^{*} \rightarrow cyclohexadienyl)^{*} \rightarrow cyclohexadienyl + cyclohexadienyl)^{*} \rightarrow cyclohexadienyl + cyclohexad$$

$$1-C_4H_3 + C_2H_2 \rightarrow (===)^* \rightarrow (phenyl)^* \rightarrow phenyl$$
(R9)

are within the uncertainty of the measurements and of the predicted rate constants; taken together, they exceed the measured net rate (formation minus destruction). On the other hand, vinyl-butadienyl combination could not be an important contributor via any of its channels, being a factor of 60 slower than the measured rate at its maximum. Then, of all the mechanisms examined in this flame, only $1-C_4H_5$ and $1-C_4H_3$ additions to acetylene can contribute to benzene formation, but by R8 and R9—direct processes involving chemically activated isomerization—not by R1-3 and R4,5.

In the butadiene flame (Figure 10), $1-C_4H_5 + C_2H_2$ or (to a lesser extent) vinyl reactions with the fuel

$$C_2H_3$$
 + butadiene → (=-CH₂-CH₂·-=)* →
=-CH₂-CH₂·-= (R10)

$$C_2H_3$$
 + butadiene \rightarrow (=-CH₂-CH₂·-=)* \rightarrow =-=-= + H
(R11)

are fast enough to account for the measured net rate of benzene formation in different regions of the flame. (As noted before, $1-C_4H_3 + C_2H_2$ reactions could not be tested because C_4H_3 had not been measured in this flame.) At the position of maximum measured rate, only R8 satisfactorily predicts the measured rate within the necessary factor of 8. Closer to the burner, where temperature is lower and butadiene concentration is still high, only R10 is consistent with the lower measured rate. Again, chemical activation effects are important, and chemically activated isomerization is required to explain the fastest rates.

Discussion

Rate Constants at Atmospheric Pressure. Rate constants for $1-C_4H_5 + C_2H_2$, $1-C_4H_3 + C_2H_2$, $C_2H_3 + 1,3-C_4H_6$, and $C_2H_3 + 1-C_4H_5$ were also calculated at 101 kPa to examine whether the same qualitative behavior in their rate constants would hold as at 2.67 kPa. To simulate combustion conditions with air, N_2 was used as the third body M with $-\langle \Delta E_{coll} \rangle = 980$ cal/mol,¹⁰ $\sigma = 3.62$ Å, and $\epsilon/\kappa = 97.5$ K.⁴⁸ Rate constant parameters are listed in Table IV.



Figure 10. Test of product-specific rate constants that could lead to benzene in 1,3-butadiene flame: measured (net) rate, \blacksquare ; $C_4H_5 + C_2H_2 \rightarrow$ benzene + H, O; $C_2H_3 + C_4H_6 \rightarrow n-C_6H_9$, \diamond ; $C_2H_3 + C_4H_6 \rightarrow 1,3,5-C_6H_8 + H$, \diamond (upper); $C_2H_3 + C_4H_6 \rightarrow c-C_6H_8 + H$, \diamond (lower); sum of predicted k's, ---.



Figure 11. Rate constants predicted for product channels of $1-C_4H_3 + C_2H_2$ at 101 kPa (1 atm), $M = N_2$.

For $1-C_4H_5 + C_2H_2$, rate constants for the chemically activated decomposition channels (H + benzene, H + $n-C_6H_6$) changed only slightly from their values at 2.67 kPa. The stabilization channels are more important because of the higher pressure, but direct benzene formation still dominated at all temperatures.

For 1-C₄H₃ + C₂H₂ (Figure 11), the rate constant for direct phenyl formation is even more dominant than at 2.67 kPa. Chemically activated adduct n-C₆H₅* can be stabilized more effectively at the higher pressure, so somewhat less is available for the other product channels. However, c-C₆H₅* also is stabilized more easily, and the isomerization is still fast. The net effect is that $k_{i/s}$ remains near $k_{a/s,\infty}$ over a greater range of temperatures. Among the other channels, adduct n-C₆H₅ is slightly favored only below 370 K, and H + n-C₆H₄ never dominates. Benzyne formation remains minor at all temperatures.

For $C_2H_3 + C_4H_6$, $k_{a/s}$ dominates up to high temperatures and remains near $k_{a/s,\infty}$. Addition/decomposition does not overtake simple addition until 1700 K, vs 1200 K at 2.67 kPa. Channels due to chemically activated isomerization were minor at 2.67 kPa and are even less important at the higher pressure.

For $1-C_4H_5 + C_2H_3$ at this pressure, simple addition becomes completely dominant. Unfavorable barriers to chemically activated

TABLE V:	Comparison of	Rate	Constants (c	:m³ mol"	⁻¹ s ⁻¹) Used	for	Aromatic	Ring	Formation
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			rate constant		
reacn from earlier study	rate expression	condition to compare ^a	earlier study	predicted, this work	
1-C ₄ H ₅ + C ₂ H ₂ reacns to n -C ₆ H ₇ , reacn 1; Cole et al. (ref 1) ^b to n -C ₆ H ₇ , reacn 1; Frenklach et al. (ref 2) ^c to n -C ₆ H ₇ , reacn 1; Frenklach and Warnatz (ref 3) ^d to benzene by overall R1-3; Colket (ref 4) ^c to benzene by overall R1-3; Harris et al. (ref 5) ^e 1-C ₄ H ₃ + C ₂ H ₂ reacns to n -C ₄ H ₄ , reacn 4; Frenklach et al. (ref 2) ^c	$10^{11.5} \exp(-3.7/RT)$ 1 × 10^{13} 1 × 10^{13} 10^{12.61} \exp(-9.0/RT) 3.2 × 10^{11} exp(-3.7/RT) ^e 1 × 10^{13}	1400 K, 2.67 kPa 1800 K, 600 kPa 1600 K, 12 kPa 1450 K, 800 kPa 1000 K, 100 kPa 2000 K, 600 kPa	8.4×10^{10} 1×10^{13} 1×10^{13} 1.8×10^{11} 5.0×10^{10} 1×10^{13}	2.4×10^{8} 2.8×10^{10} 6.5×10^{8} 2.9×10^{11} 1.2×10^{11} 3.4×10^{10}	
to $n \cdot C_6H_5$, reacn 4; Frenklach and Warnatz (ref 3) ^d to $n \cdot C_6H_5$, reacn 4; Colket (ref 4) ^{c,f} to phenyl by overall R4,5; Harris et al. (ref 5) ^e	$\frac{1 \times 10^{13}}{10^{4.63} T^{1.97}} \exp(+5.6/RT)$ 7.0 × 10 ¹¹	1700 K, 12 kPa 1750 K, 800 kPa 1525 K, 100 kPa	1×10^{13} 5.2 × 10 ¹¹ 7.0 × 10 ¹¹	2.7×10^{8} 5.8×10^{10} 1.3×10^{11}	

^a Third body taken as Ar, except CO in study of Cole et al. (ref 1). ^b 1,3-Butadiene/ $O_2/3.0\%$ Ar laminar, premixed flame with C/O ratio 0.87. ^c Shock tube pyrolysis of dilute hydrocarbon in argon. ^d C₂H₂/ $O_2/55.0\%$ Ar laminar, premixed flames with C/O ratio 1.10. ^cC₂H₄/ O_2 /Ar laminar, premixed flames with C/O ratio 5.52, 2.76, and 3.00.

channels combine with faster collisional stabilization to keep $k_{a/s}$ near $k_{a/s,\infty}$.

General Reinterpretation of Literature Tests. As the actual molecular behavior is so different from the routes of previous workers, it may seem surprising that $1-C_4H_5 + C_2H_2$ and $1-C_4H_3$ + C_2H_2 had been identified before as key reactants. The main reason was that reactive associations $1-C_4H_5 + C_2H_2 \rightarrow n-C_6H_7^*$ and $1-C_4H_3 + C_2H_2 \rightarrow n-C_6H_5^*$ were the rate-determining steps in R7 and R8 at most conditions that have been tested.

In a series of steps, the slowest step is rate-determining. Reactions 1-3 are a thermal series, and previous workers have used k_{∞} for R1 ($k_{a/s,\infty}$ for 1-C₄H₅ + C₂H₂ \rightarrow n-C₆H₇) and for R2 and R3 if included. Reaction 1 then was found to be rate-determining for benzene formation, by estimation¹ or by calculation,³ or it was assumed to be rate-determining.^{4.5} The same approaches were used for phenyl formation,²⁻⁵ and R4, the implicitly high-pressure-limit addition step, was calculated²⁻⁴ or assumed⁵ to be rate-determining. Falloff makes R1 and R4 even slower—too slow to account for benzene formation here.

In contrast, among parallel channels, the fastest step is ratedetermining. Four parallel channels to thermalized products—R1, R6, R7, and R8—are expected from $1-C_4H_5 + C_2H_2$. Reaction 8, direct formation of benzene, is seen to be fastest and thus rate-determining because it has the highest rate constant. This "elementary" reaction is a series of steps, though, just like any bimolecular association or unimolecular reaction. Its rate constant $k_{i/d}$ is near $k_{a/s,\infty}$ because the characteristic rates of conversion between $n-C_6H_7^*$ and $c-C_6H_7^*$ and from $c-C_6H_7^*$ to H + benzene are much faster than the rate of reactive association between $1-C_4H_5$ and C_2H_2 , forming the initial population of $n-C_6H_7^*$. In the same way for $1-C_4H_3 + C_2H_2$, it is the association event forming $n-C_6H_5^*$, not $n-C_6H_5$, that is rate-determining.

At high temperatures, this good fortune does not necessarily hold, as illustrated by $1-C_4H_3 + C_2H_2$. Interpretation as in the paragraph above applies at lower temperatures, but despite favorable conditions for forming $c-C_6H_5^*$ (phenyl*), stabilization is still necessary. Figures 6 and 11 show $k_{i/s}$ for phenyl formation beginning to drop off rapidly from $k_{a/s,\infty}$ at higher temperatures. There $\beta Z[M]$ is lower, allowing decompositions to divert $n-C_6H_5^*$ to $H + n-C_6H_4$ ($k_{a/d}$) and to $1-C_4H_3 + C_2H_2$ (falloff in $k_{a/s}$). Use of $k_{a/s,\infty}$ would overpredict direct phenyl formation if R4.5 were taken to be overall with R4 rate-limiting.

Specific Reinterpretation of Literature Tests. More detailed examination of literature tests shows exactly the contrast with this new understanding. As a basis for discussion, rate constant expressions from the earlier studies are evaluated at conditions of reported maximum contribution or rate and compared in Table V to rate constants from bimolecular quantum-RRK at the same conditions.

Consider rate constants for the routes that have been tested before with apparent success, beginning with $1-C_4H_5 + C_2H_2$:

(i) The rate constant of Cole et al.¹ is smaller than $k_{a/s,\infty}$ estimated here because ΔC_p^* contributions were included in the

present calculations. Falloff makes the actual $k_{a/s}$ lower by a factor of 350 from the earlier value (Table V), but the chemically activated, direct channel to benzene keeps the rate constant approximately equal to $k_{a/s,\infty}$ (see Figure 5). Thus, even though the assumed pathway R1-3 via thermalized intermediates is not feasible, a number of the right order of magnitude was used because falloff was neglected.

(ii) Frenklach and co-workers chose a rate constant of 1×10^{13} cm³ mol⁻¹ s⁻¹ for R1 in order to be at a collision-frequency upper limit, while $k_{a/s,\infty}$ is a factor of 20 lower by the estimate here. Reaction 1 was also assumed to be at the high-pressure limit at 500-800 kPa in the shock tube,² but falloff lowers $k_{a/s}$ further to be a factor of 360 less than 1×10^{13} (Table V). The flame studies³ were at much lower pressures, so falloff was even more severe, making $k_{a/s}$ lower than their value by 4 orders of magnitude. Similarly to i, though, direct aromatics formation proceeds with a rate constant ($k_{i/s}$) near $k_{a/s,\infty}$. Sensitivity to thermodynamics was also noted by Frenklach and Warnatz,³ but it is less important in the nearly irreversible R8.

(iii) Colket⁴ assumed a thermal pathway R_{1-3} but modeled it as an overall reaction to benzene. Interestingly, at the condition where this overall reaction was predicted to be important, he chose a rate constant expression to fit his shock tube data that gives numbers close to the values estimated here (see Table V).

(iv) Harris et al.⁵ used the rate constant of Cole et al.¹ directly and wrote the pathway of R1-3 as an overall reaction. Again, although addition in the high-pressure limit was assumed incorrectly, their choice of this expression for the hypothetically rate-limiting step made their $k_{a/s}$ (R1) only slightly slower than the correct $k_{i/d}$ (R8; see Table V).

For $1-C_4H_3 + C_2H_2$, addition/stabilization and direct phenyl formation may be compared similarly except for one major difference. Direct phenyl formation is a stabilization channel too, so low pressures and high temperatures strongly inhibit it, like $n-C_6H_5$ formation but unlike R8. The rate constant reaches a maximum at 1150 (2.67 kPa, Figure 6) to 1450 K (101 kPa, Figure 11), which would limit its importance at higher temperatures.

Direct phenyl formation dominates the product channels at many of the conditions examined and has a rate constant close to $k_{a/s,\infty}$. Again, the upper-bound addition rate constant of Frenklach and co-workers^{2,3} is much higher than the rate constant predicted here (Table V). Their sensitivity analysis may also have been affected by this difference (they varied rate constants only by a factor of 5), but the importance of $1-C_4H_3 + C_2H_2$ reaction—via chemically activated isomerization—is supported by the present work. Colket⁴ also wrote R4 and R5 separately with a lower k_{∞} for R4. Poor stabilization and diversion of *n*- $C_6H_5^*$ into addition/decomposition reduce $k_{a/s}$ (and $k_{i/s}$) below k_{∞} (Table V). Harris et al.⁵ chose to write R4,5 as an overall reaction and adjusted the rate constant to fit their benzene data. Their result is within a factor of 5 of the $k_{i/s}$ (R7; Table V) predicted here. $C_2H_3 + C_4H_4$ seems unlikely as a route to aromatics. Colket⁹ hypothesized that these reactants might lead to benzene by the reactions

$$C_2H_3 + C_4H_4 \rightarrow \text{linear } C_6H_7 \rightarrow \text{cyclic } C_6H_7 \rightarrow \text{benzene} + H$$

(R10,11,12)

Falloff was not considered although it would slow this thermal sequence. The present study only finds that $C_2H_3 + C_4H_4$ was unimportant in the flames studied here, while chemically activated reactions involving C_4H_4 could be more important in C_4H_4 pyrolysis because much more C_4H_4 is available. However, one problem in pathway R10-12 is that critical H-shift steps are omitted, as recognized by Colket. The linear C_6H_7 adduct is not $n-C_6H_7$ (=====*, as formed from $1-C_4H_5 + C_2H_2$); instead it is ===*=* or its resonance structure ====**. A 1,3-H shift would be required to form the more easily cyclized $n-C_6H_7$. An alternative complication is that radical self-addition of ====** would form a strained allenic ring or its resonance structure 1,5-cyclohexadienyl—not the c- C_6H_7 (2,4-cyclohexadienyl) formed from $1-C_4H_5 + C_2H_2$. Again, H shifts would be necessary to form benzene.

Energy-Transfer Analysis. A state-to-state energy-transfer model was used to examine the β approximation. Difficulty in collisional stabilization is the main reason that chemically activated isomerization R9 to phenyl and isomerization/decomposition R8 to benzene are important, and a master-equation model should describe the competition more realistically.

A collision-efficiency relationship⁴⁹ from unimolecular reaction theory was used above to estimate β . In that formula, the relative population at the barrier, F_E , was approximated here as 1.15. Higher values of F_E are more realistic for large molecules at high temperatures, so the approximation would seem to overestimate stabilization. However, use of β is not strictly correct because it was derived for single-channel unimolecular decomposition. Full master-equation treatment of chemically activated processes is still under development.⁵⁰

Rate constants for product channels of $1-C_4H_3$ and $1-C_4H_5$ + C_2H_2 were calculated with an approach described by Dean,⁴⁰ adapted here to include chemically activated isomers. Reaction kinetics mechanisms were constructed by treating each chemically activated state $A^*(E_k)$ and $I^*(E_k)$ as distinct species separated from E_{k+1} and E_{k-1} by $\Delta E = h \langle v \rangle$. "Species" $A^*(E_k)$ were formed from reactants with a rate constant $k_{a/s,\infty} f(E_k,T)$, while rate constants $k(E_k)$ for decompositions and isomerizations of $A^*(E_k)$ and $I^*(E_k)$ were calculated with the quantum-RRK equation. Rates for transitions between consecutive states were based on the total rate of up and down transitions away from E_k being given by collision-frequency rate constants Z_{LJ} . For the C₄H₃ case, contributions from 37 energy levels were considered ($\Delta E = 2810$ cal/mol; 82 "species" and 362 reactions), while 39 levels were analyzed for C_4H_5 ($\Delta E = 3430$ cal/mol; 85 "species" and 382 reactions). Finally, the mechanisms were integrated with LSODE and CHEMKIN software packages.⁵¹

Rate constants predicted for the dominating phenyl and benzene formation channels were very close. For the state-to-state model, the rate of product formation over 0.1 ms was divided by both reactant concentrations to give an effective second-order rate constant. Calculations in previous sections (β model) at 1500 K and 2.67 kPa gave a phenyl formation rate constant of 2.3 × 10¹¹ mol cm⁻³ s⁻¹, compared to 1.8 × 10¹¹ by the state-to-state calculations. Rate constants for benzene from 1-C₄H₅ + C₂H₂ were still closer to each other, 2.3 × 10¹¹ vs 2.4 × 10¹¹.

Of even greater interest, the state-to-state model indicated that collisional stabilization is even more difficult than predicted by the weak-collision model, so chemically activated decompositions are even more important, much as has been found in the absence

TABLE VI: Comparison of Weak-Collision β Model to State-to-State Energy-Transfer Model of Collisional Energy Transfer in Chemically Activated Isomerizations at 1500 K, 2.67 kPa

branching ratios for	weak-collision model	state-to-state model	
$1-C_4H_3 + C_2H_2$ reactions			
$[n-C_6H_5]_{a/s}[phenyl]_{i/s}$	2.8×10^{-3}	5.5 × 10 ⁻⁶	
$[n-C_6H_4]_{a/d}/[phenyl]_{i/s}$	0.038	0.060	
[benzyne] _{i/d} /[phenyl] _{i/s}	0.091	0.23	
$1-C_4H_5 + C_2H_2$ reactions			
$[n-C_6H_7]_{a/s}/[benzene]_{i/d}$	0.0151	1.23×10^{-7}	
$[n-C_6H_6]_{a/d}/[benzene]_{i/d}$	0.118	0.117	
$[c-C_6H_7]_{i/s}/[benzene]_{i/d}$	3.6×10^{-4}	7.7 × 10-9	

of chemically activated isomerization.⁴⁰ Table VI shows this effect in branching ratios relative to the dominant channels, phenyl production (isomerization/stabilization) for $C_4H_3 + C_2H_2$ and direct benzene production (isomerization/decomposition) for C_4H_5 + C_2H_2 . For $C_4H_3 + C_2H_2$ at these conditions, decompositions to $n-C_6H_4$ and benzyne become slightly more important while remaining slower than phenyl stabilization. Addition/stabilization to $n-C_6H_4$ becomes less important than before because entropic and energetic effects can drive adduct A* further toward isomer I*. For $C_4H_5 + C_2H_2$, the dominant channel is still a chemically activated decomposition, so other channels become even less important when stabilization of A* and I* is more difficult. For addition/decomposition, the effect is minor, but the two stabilization channels are predicted to be slowed by 5 orders of magnitude.

Conclusions

In two flames, the highest rates of benzene formation were shown to be reasonably accounted for by radical additions of $1-C_4H_5$ and $1-C_4H_3$ to C_2H_2 , but production of the aromatic ring is direct rather than through thermal intermediates. The cause is chemical activation of the initial adduct, which has not been recognized before in aromatics formation. Because no thermal intermediates are involved, they cannot be destroyed en route to the aromatic ring. Vinyl addition to butadiene may also contribute when butadiene is the fuel.

Additions of $1-C_4H_3$ and $1-C_4H_5$ to acetylene (and to other alkynes) have certain notable advantages:

(1) Most significantly, chemically activated isomerization is strongly favored because these particular cyclic isomers are much more stable than the thermalized linear adducts. This stability inhibits chemically activated reisomerization and overcomes the entropy loss from cyclization.

(2) The energy in the chemically activated adducts greatly exceeds the thermal barrier to isomerization. Cyclization can take place directly by low-activation-energy, radical self-addition within the adducts. In contrast, an intermediate H-shift step must occur when C_2H_3 adds to alkynes, and high-activation-energy molecular cyclization is necessary for 1,3,5-hexatriene.

(3) The conjugated π bonds of these linear adducts add to their thermal stability.

(4) No bimolecular abstraction or addition of H is necessary to form an aromatic species.

Roles for C_3H_3 and C_3H_4 seemed unlikely but will be examined further by using C_3H_4 flames. Similarly, the $C_2H_3 + C_4H_4$ pathway proposed by Colket⁴ deserves more study. Further work is under way in our laboratories to study aromatics formation in other flames and in pyrolysis and to clarify the formation and destruction kinetics of the precursor C_4 radicals.

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Registry No. C_2H_2 , 74-86-2; c-C₆H₆, 71-43-2; 1,3-C₄H₆, 106-99-0; 1-C₄H₅, 86181-68-2; 1-C₄H₃, 2810-61-9; C₂H₃, 2669-89-8; *n*-C₆H₆, 10420-90-3; c-C₆H₇, 12169-67-4; *n*-C₆H₅, 108773-39-3; c-C₆H₅, 2396-01-2; 1,3,5-C₆H₈, 2235-12-3; c-C₆H₉, 53175-87-4; c-C₆H₈, 29797-09-9; c-C₆H₄, 462-80-6; 1,3,5-C₆H₇, 123411-84-7.