

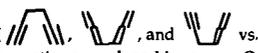
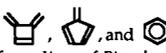
C₃H₃ REACTION KINETICS IN FUEL-RICH COMBUSTION

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Keywords: propargyl, chemical activation, benzene

ABSTRACT

At typical flame temperatures and pressures, we predict that direct propargyl (C₃H₃) combination forms the open-chain C₆H₆ species 1,5-hexadiyne, 1,2,4,5-hexatetraene, and 4,5-hexadienyne in preference to cyclic C₆H₆ species 3,4-dimethylenecyclobutene, fulvene, and

benzene (, and ). These chemically activated reactions, analyzed by a new Q-formalism of Bimolecular Quantum-RRK, have rate constants and rates that are consistent with C₆H₆ data from a C₂H₂/O₂/Ar flat flame. Cyclic C₆H₆'s may then be generated by thermal isomerizations.

INTRODUCTION

Recently, C₃H₃ has been the subject of intense interest as a possible precursor to aromatics in flames.¹⁻⁸ In earlier work, Hurd and co-workers proposed in 1962 that aromatics might be formed by combination of trimethine (CHCHCH)⁹, and Tsang had encouraged others to explore propargyl (·CH₂-C≡CH or CH₂=C=CH·) as an aromatics precursor based on his high soot yields from pyrolysis experiments.¹⁰ Kern and co-workers provided the first experimental evidence and mechanism for C₆H₆ formation from C₃H₃,^{1,2} stimulating much of the subsequent research.

In 1989 we proposed⁴ a chemically activated pathway from C₃H₃ to benzene (Figure 1), similar to that of Kern, and presented preliminary calculations of its feasibility. The electron density of propargyl is best represented as propynyl³ although it is a resonance structure of propynyl and propadienyl (CH=C-CH₂· and ·CH₂=C=CH₂). Propynyls may combine to make chemically activated 1,5-hexadiyne ("hot" 1,5-hexadiyne). The hot adduct may isomerize by a Cope rearrangement to hot 1,2,4,5-hexatetraene, which may isomerize to make hot 3,4-dimethylenecyclobutene (DMCB) by a sigmatropic ring closure analogous to that of 1,3-butadiene forming cyclobutene. DMCB can isomerize to hot fulvene (methylenecyclopentadiene) which can isomerize to hot benzene. Because of chemical activation, the energy released into the first adduct by bond formation, each of these steps occurs above the intrinsic or thermal energy barriers. Each one of these chemically activated isomers may be stabilized by bimolecular collisions, or it may decompose or isomerize unimolecularly. This hypothesized route was based on thermal pyrolyses of 1,5-hexadiyne to DMCB, fulvene, and benzene;¹¹⁻¹⁵ pyrolysis of hexatetraene to the same products;¹⁴ pyrolysis of DMCB to fulvene and benzene;¹⁵ and pyrolysis of fulvene to benzene.^{15,16} Compared to the route of Kern and coworkers,² this route could proceed without thermal intermediates and without diradicals.

Independently and at the same time, and Stein developed a route similar to that in Figure 1,⁵ and Alkemade and Homann proposed a fourth, quite different route.³ Stein pyrolyzed 1,2-hexadiyne at different temperatures in a VLPP reactor. At low temperatures, DMCB was formed, while at higher temperatures, fulvene and benzene were formed apparently from a DMCB intermediate; Stein proposed that parallel paths to the two products may occur. Alkemade and Homann have made the only direct experimental studies of C₃H₃ combination, finding a mixture of products including benzene. Their mechanism involved cyclopropenyl intermediates similar to those proposed as intermediates in propyne/propadiene isomerization.¹⁷

More recently, Miller and Melius⁷ have proposed a fifth route via 4,5-hexadienyne, the head-to-tail combination product of propargyls. They suggest rearrangement of the acetylenic group to a vinylidene form, which would insert into an allenic C-H bond to form a 1,2,4-cyclohexatriene. Finally they suggest rapid rearrangement to benzene, apparently by a molecular 1,3 H-shift.

Most of these routes are energetically feasible, but there are energetic and entropic challenges to overcome en route. Direct closure to a six-membered ring requires a tight transition state with loss of internal rotation(s), and 1,2- or 1,3-H-shifts and cyclization to four- or five-membered rings is even tighter. The overall exothermicity in forming benzene is a strong driving force, but the intermediate steps must be successful as well. Calculations are presented here for the mechanism of Figure 1. The formation of thermal intermediates is predicted to play more of a role than in C₄H₃ and C₄H₅ additions to C₂H₂, where the low A-factors (entropic difficulty) are compensated for by low energy barriers to cyclization.

CALCULATIONAL METHODS

Multiple isomerizations require a new form of chemical-activation analysis, so we have developed¹⁸ a "Q-formalism." Some discussion of the form and nomenclature serves to clarify the process of multiple chemically activated isomerization. The *i*th isomer can be designated either as being in a specific energy state, $I_i(E)$, or as being the thermal species I_i (species in a thermal distribution). High-energy states $I_i(E)$ may be collisionally stabilized by a third-body gas, or they may decompose or isomerize unimolecularly.

Consider Figure 1. Propynyl combination forms different quantum states $I_i(E)$ of 1,5-hexadiyne ($i=1$) with a rate constant $k_{\infty}f(E, T)$, where k_{∞} is the high-pressure-limit rate constant for reactants forming the thermal adduct I_1 and $f(E, T)$ is the chemical-activation distribution function. With sufficient energy, $I_1(E)$ may:

- Be stabilized by a third-body gas M into a thermal distribution I_1 at a rate $\beta_1 Z_1 [M] \cdot [I_1(E)]$;
- Decompose to new products like $H + \dots =$ at a rate $(k_{dec}(E))_{ij} \cdot [I_i(E)]$; where j is one of $J(i)$ decomposition channels;
- Isomerize to $I_2(E)$ (1,2,4,5-hexatetraene) with a rate $(k_f(E))_i \cdot [I_i(E)]$; or
- Revert - just a decomposition channel for the first isomer, the adduct, but designated for generality as if it were a reverse isomerization with a rate of $(k_r(E))_i \cdot [I_i(E)]$.

Likewise, $I_2(E)$ may isomerize in turn to $I_3(E)$ (3,4-dimethylencyclobutene), $I_4(E)$ (fulvene), and $I_5(E)$ (benzene). Each $I_i(E)$ may be stabilized to I_i , decompose, isomerize to the next isomer, or revert to the previous isomer.

The rate constants have a compact form incorporating a recursive term Q_i . Here we show a Quantum-RRK form, where the energy variable, quantized relative to the bottom of the first energy well, is $n = E / h \langle v \rangle$:

$$k(C_3H_3 + C_3H_3 \rightarrow I_1) = \sum_{n=E/h\langle v \rangle = m_{-1}}^{\infty} \beta_1 Z_1 [M] \cdot \prod_{i=0}^n (Q_i(E)) \quad [1]$$

$$k(C_3H_3 + C_3H_3 \rightarrow P_j + P'_j) = \sum_{n=m_{-1}}^{\infty} (k_{dec}(E))_{ij} \cdot \prod_{i=0}^n (Q_i(E)) \quad [2]$$

$$Q_i(E) = \frac{k_{source}}{\beta_1 Z_1 [M] + \sum_{j=1}^{J(i)} (k_{dec}(E))_{ij} + (k_f(E))_i + (k_r(E))_i - (k_r(E))_{i+1} Q_{i+1}} \quad [3]$$

where m_{-1} is the quantized barrier for reversion of I_1 to reactants;

$k_{source} = k_{\infty}f(E, T)$ for $i=1$ or $(k_f(E))_{i-1}$ for $i>1$; and
 $(k_f(E))_i = 0$ and $(k_r(E))_{i+1} Q_{i+1} = 0$ for $i=N$.

Energy-dependent rate constants $k(E)$ for the *i*th isomer are calculated relative to the bottom of the energy well for that isomer,¹⁹ but the summations of Equation 1 and 2 are over the energies of the chemically activated adduct.

High-pressure-limit Arrhenius parameters of the different steps are the key input parameters for the calculations. Parameters in one direction are often available or may be estimated, but thermochemistry is necessary to obtain parameters in the opposite direction. Thermochemistry used here is summarized in Table I, and the resulting set of A-factors and activation energies is presented in Table II. Other parameters necessary for the calculations include mean frequency of the isomers (1010, 1240, 1176, 1209, and 1205 cm^{-1} for $i=1$ to 5, respectively); molecular weight of 78.06; Lennard-Jones parameters $\sigma = 5.27 \text{ \AA}$ and $\epsilon/\kappa = 440 \text{ K}$; and molecular weight, Lennard-Jones parameters, and collisional step-down size for the third-body gas M .

RESULTS

At high pressure (1 atm, Figure 2a) and low pressure (600 Pa, Figure 3a), C_3H_3 combination as propynyls is predicted to form the thermal adduct as its dominant channel. This result is somewhat surprising, as there is

no intrinsic energy barrier to proceeding all the way to benzene or to phenyl and H. On the other hand, while the chemically activated adduct can go over the isomerization energy barrier, entropy loss in the tight transition state is a serious limitation, as manifested in the low *A*-factor. At its lowest energy level (the ground energy of the reactants), the hot adduct has 29 kcal/mol available for isomerization, but the *A*-factor, which limits *k*(*E*), is only $3 \cdot 10^{11}$ and the energy gain in isomerization is only 1 kcal/mol. Stabilization of the adduct is then relatively easy. At higher energy levels, reached at higher temperatures, the *A*-factors favor reversion to reactants by a loose transition state. Phenyl contributes only slightly, and then only at 600 Pa and the highest temperatures; DMCB is the dominant thermal product, which may rapidly, thermally isomerize.⁵

Once 1,5-hexadiyne forms, it may isomerize thermally to benzene. Likewise, the next most important products, 1,2,4,5-hexatetraene and 3,4-dimethylcyclobutene may form benzene thermally.

Combination as propadienyls should be much less favorable. Radical density is greatest on the CH₂ group within C₃H₃, corresponding to propynyl, and C₃H₃ tends to react as propynyl.⁵ If C₃H₃ had 10% propadienyl character, the probability of propadienyl+propadienyl combination would only be 1% of the total combination rate. Again, though, thermal isomerization of the products would be possible. Also, head-to-tail combination (propynyl + propadienyl) forms 4,5-hexadiynene, which may isomerize to benzene thermally.²⁹

These results would agree with the experimental results of Alkemade and Homann³ only if thermal isomerization contributed, but there is no conflict with the C₂H₂/O₂/Ar flame data of Westmoreland et al.³⁰ The predicted rate constants would easily account for the rate of C₆H₆ production in that flame, as molecular-beam mass spectrometry does not resolve isomers of mass 78. Also in that work, a microprobe sample of the stable species was collected downstream of the region of high C₆H₆ production rate. GC/MS analysis using aDB-5 fused-silica column identified four isomers of mass 78 at concentrations of 6, 1.3, 20 (for benzene), and 0.4 ppmv in the flame. Future work in our laboratory will examine the isomer split throughout this flame.

Another possible cause of discrepancy is uncertainty in the input barriers. Stein inferred a rate constant of $8 \cdot 10^{12} \exp(-50.0/RT)$ for DMCB pyrolysis to fulvene and benzene.⁵ Using these alternative parameters for DMCB → fulvene, little change in the largest rate constants is predicted at 1 atm. In contrast, direct formation of phenyl contributes much more significantly at 600 Pa and the highest temperatures, although the thermal path is also predicted to dominate at lower temperatures. Again, having no intrinsic barrier is helpful, but entropic limitations are also very important.

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grants No. CTS-88-10562 and CTS-9057406, by the Exxon Education Foundation, and by the General Electric Company. The Government has certain rights in this material.

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Table I: Thermodynamic properties of species used in the analysis (1 atm standard state).

Species and structures	ΔH_f° ₂₉₈ (kcal/mol)	S° ₂₉₈ (cal/mol K)	Source
Propargyl, C ₃ H ₃	81.4	60.6	ΔH_f° of McMillen and Golden (Ref. 20); S°_{298} estimated.
1,5-hexadiyne ()	99.0	81.3	ΔH_f° of Rosenstock et al. (Ref. 21), compared to 99.5 by group additivity; S°_{298} by group additivity.
1,2,4,5-hexatetraene ()	98.0	78.6	ΔH_f° of Rosenstock et al. (Ref. 21), compared to 94.5 by group additivity; S°_{298} by group additivity.
Dimethylenecyclobutene ()	80.4	68.4	ΔH_f° of Roth et al. (Ref. 22); S°_{298} from statistical mechanics using literature moments (Ref. 23) and frequencies assigned by analogies with fulvene.
Fulvene ()	53.5	67.9	ΔH_f° of Roth et al. (Ref. 22), compared to 45.4 by group additivity; S°_{298} from statistical mechanics using literature frequencies (Ref. 24) and moments (Ref. 23).
Benzene ()	19.8	64.3	Benson (Ref. 25).
Phenyl	78.5	69.4	ΔH_f° of McMillen and Golden (Ref. 20); S°_{298} of Benson (Ref. 25).
H-atom	52.1	27.4	Benson (Ref. 25).

Table II: High-pressure-limit rate constants for steps in the $C_3H_3 + C_3H_3$ reaction set. A -factors are in cm^3, mol, s units; E_{act} 's are in kcal/mol.

Reaction	k_{fwd}		k_{rev}		Sources
	A_{fwd}	$E_{a,fwd}$	A_{rev}	$E_{a,rev}$	
 → 2 C_3H_3	$6.6 \cdot 10^{17}$	63.2	$3.1 \cdot 10^{13}$	0.0	k_{rev} from $k(C_3H_3 + C_3H_3) = 3.4 \cdot 10^{13}$ by measurements of Alkemade and Homann (Ref. 3) assuming C_3H_3 had 90% propynyl character; k_{fwd} from K_c .
 → 	$3.0 \cdot 10^{11}$	34.4	$1.15 \cdot 10^{12}$	35.4	k_{fwd} from fit to data of Huntsman and Wristers (Ref. 11).
 → 2 C_3H_3	$2.8 \cdot 10^{16}$	64.2	$3.4 \cdot 10^{11}$	0.0	k_{rev} from $k(C_3H_3 + C_3H_3) = 3.4 \cdot 10^{13}$ by measurements of Alkemade and Homann (Ref. 3) assuming C_3H_3 had 10% propadienyl character.
 → 	$3.4 \cdot 10^{11}$	15.9	$5.8 \cdot 10^{13}$	33.5	k_{rev} by analogy to $k(\text{cyclobutene} \rightarrow 1,3\text{-butadiene})$ of Jasinski et al. (Ref. 27).
 → 	$3 \cdot 10^{13}$	66	$3.9 \cdot 10^{13}$	93.	k_{fwd} by analogy to $k(\text{fulvene} \rightarrow \text{benzene})$; see text for comparison to $8 \cdot 10^{12} \exp(-50.0/RT)$ of Stein (Ref. 5).
 → 	$3 \cdot 10^{13}$	66	$1.8 \cdot 10^{14}$	100	k_{fwd} from midrange of Arrhenius parameters of Gaynor et al. (Ref. 16).
 → H + Phenyl	$1.8 \cdot 10^{16}$	110.2	$2.2 \cdot 10^{14}$	0	k_{rev} from k_{300} of Ackermann et al. (Ref. 28).

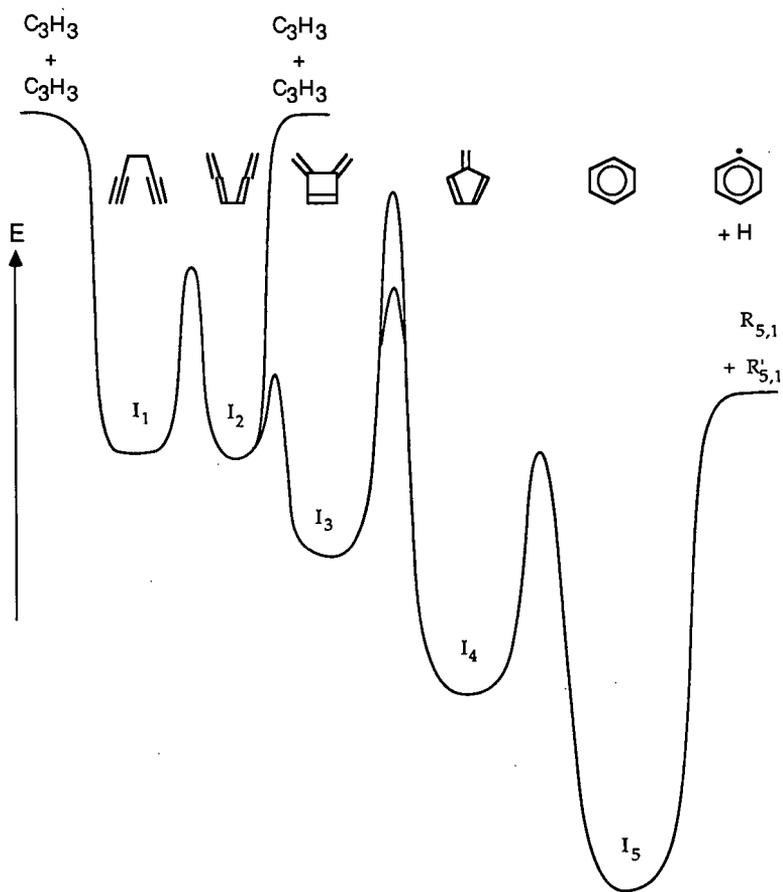


Figure 1. Energy diagram for propargyl combination, subsequent isomerizations, and decompositions.

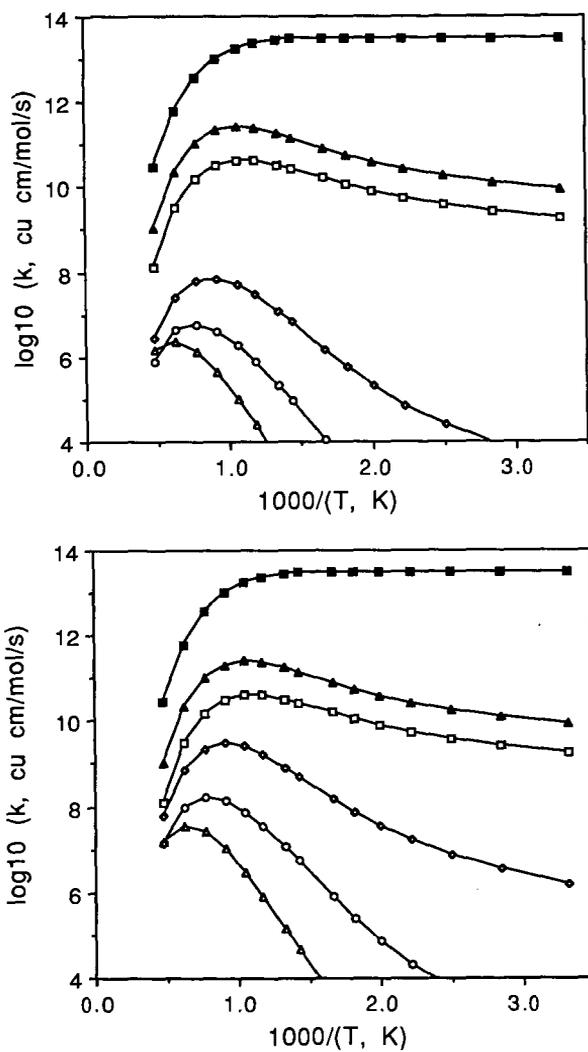


Figure 2. Arrhenius plot at 1 atm of predicted rate constants for $C_3H_3 + C_3H_3$ combining as propynyls: (top) using 66 kcal/mol barrier for DMCB to fulvene, (bottom) using 50 kcal/mol barrier of Stein (Ref. 5). Product channels: 1,5-hexadiyne ■, 1,2,4,5-hexatetraene ▲, 3,4-dimethylenecyclobutene □, fulvene ○, benzene O, H + phenyl △.

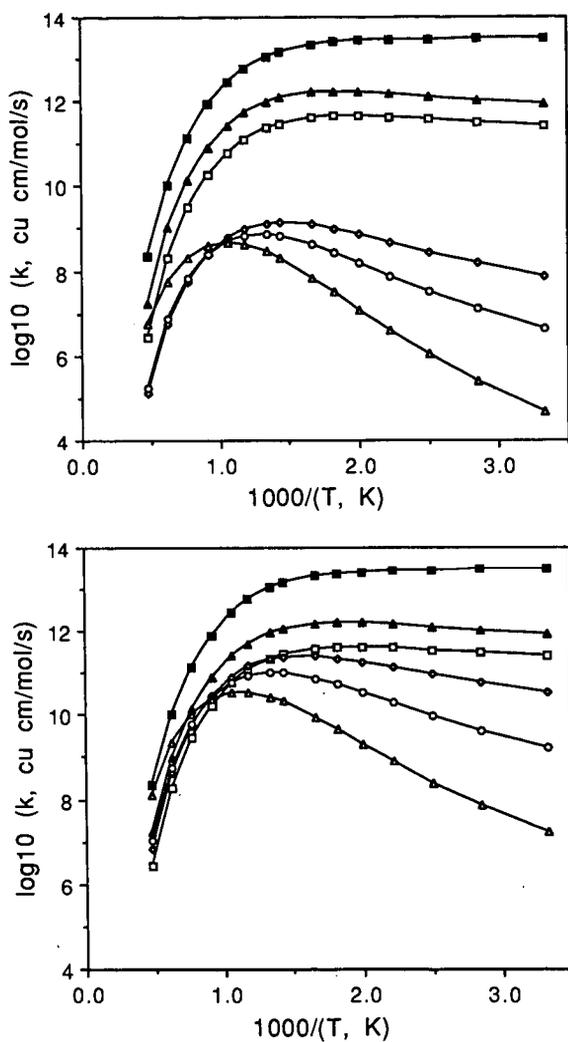


Figure 3. Arrhenius plot at 600 Pa of predicted rate constants for $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ combining as propynyls: (top) using 66 kcal/mol barrier for DMCB to fulvene, (bottom) using 50 kcal/mol barrier of Stein (Ref. 5). Product channels: 1,5-hexadiyne ■, 1,2,4,5-hexatetraene ▲, 3,4-dimethylenecyclobutene □, fulvene ◇, benzene ○, H + phenyl △.