

MASTER EQUATION CALCULATIONS FOR HYDROCARBON AND NITROGENOUS SPECIES REACTION RATE CONSTANTS AT LOW PRESSURES AND TEMPERATURES

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Titan's cold hydrocarbon surface and hazy lower atmosphere from Huygens.

Jovian planet photochemistry starts very high up with Lyman- α photolysis of methane and subsequent reactions, at very low temperature (60K) & pressure (1 μ bar).

Pressure dependent radical recombination (and chemical activation) reactions are particularly important in outer planet atmospheres, especially those involving H or CH₃, because they usually have no energy barrier.

1. Methods
2. Benzene formation and photolysis
3. H addition, tunneling, infrared (IR) radiative stabilization
4. Chemical activation and supercollisions: $\text{H} + \text{C}_3\text{H}_7$
5. $\text{NH}_2 + \text{CH}_2\text{CN}$
6. Haze precursor steps



Low pressure rates can be very temperature dependent.

$$k_{\text{diss}} = k_1[M] k_2 / (k_{-1}[M] + k_2) \quad k_{\text{recomb}} = (K_{\text{EQ}}) k_{\text{diss}}$$

IF we can determine rates at each energy for the competing steps, rate constants can be calculated for a pressure P and initial energy distribution (temperature) using time-evolving behavior of the Master Equation:

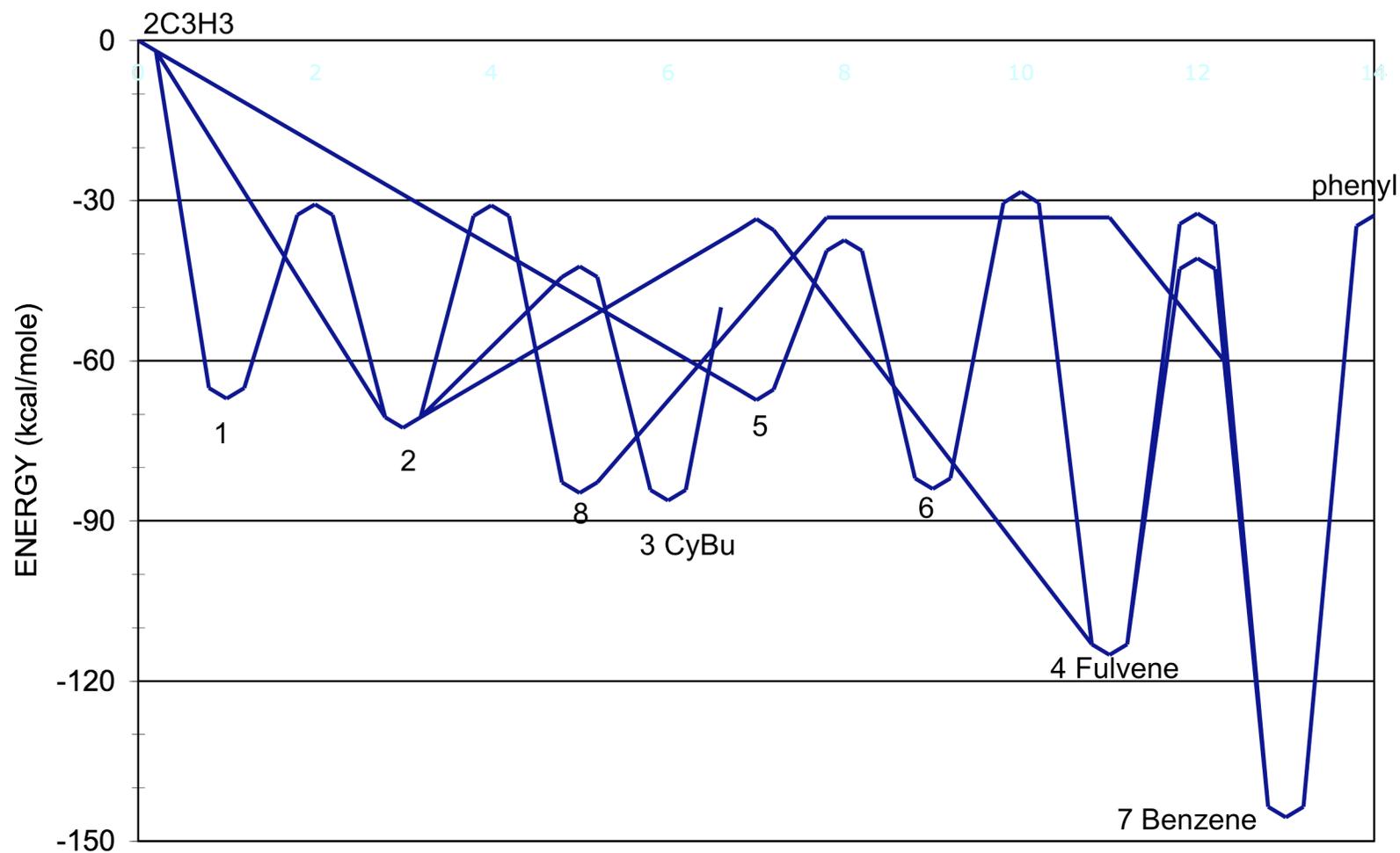
$$k_I(E) = \sum k_{JI}(E) - k_{IJ}(E) - k_M(E) + k_M(E',E)n(E')$$

- Collisional energy transfer rates $k_M(E, E')$ are determined from ΔE parameter.
- Chemical rate from species I to species or product J are computed by transition state theory according to the configuration describing when reaction occurs.
- Use potential energy surface information, fit room T data, calculate for lower T

Use John Barker's MultiWell code

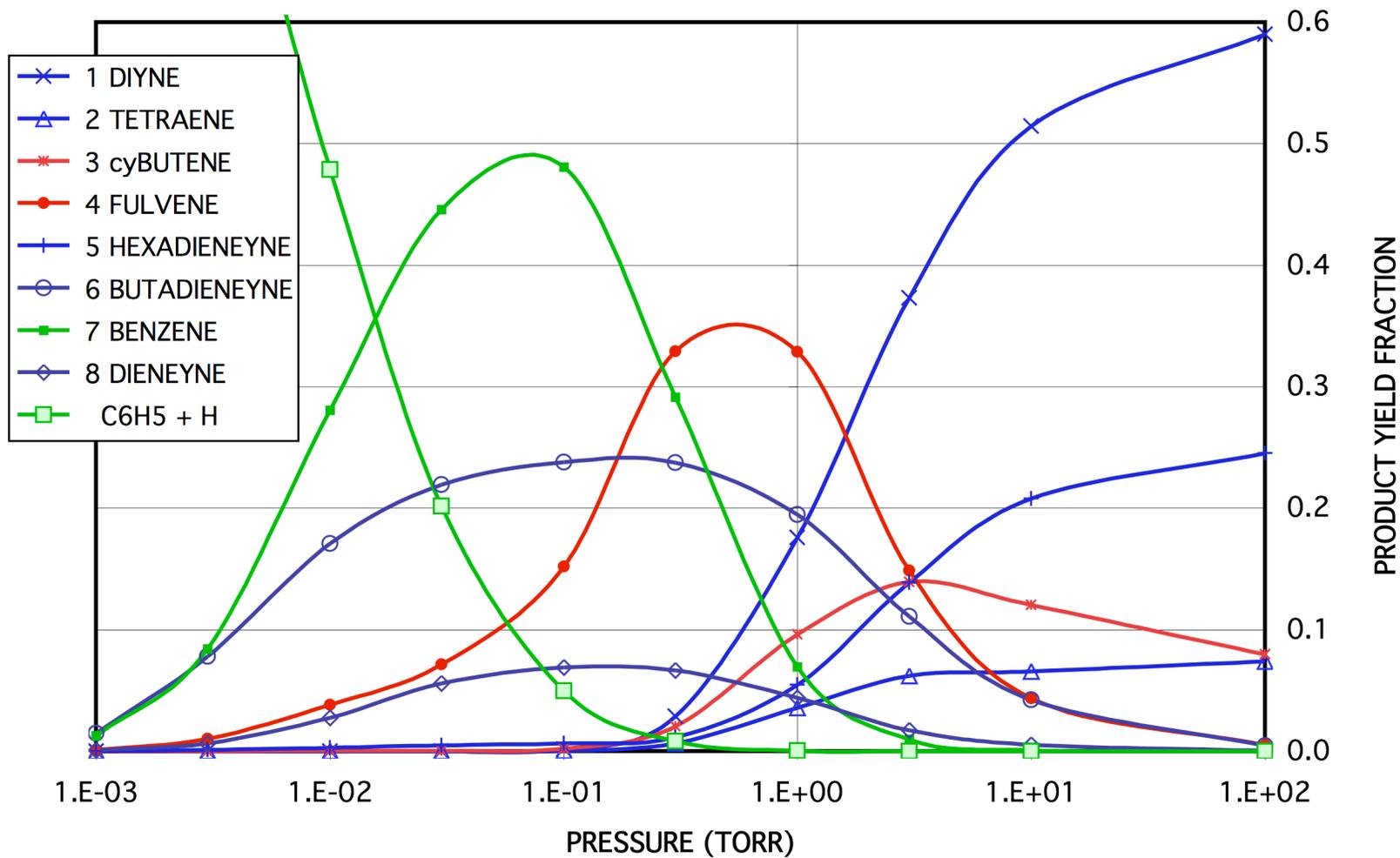
Benzene has been observed in atmospheres of Jupiter, Saturn, Neptune, and Titan.
First aromatic and a precursor to condensates.

PROPARGYL - BENZENE POTENTIAL SURFACE: MILLER & KLIPPENSTEIN
TS PARAMETERS THAT FIT DATA J. Phys. Chem. A 107, 7783-7799 (2003)

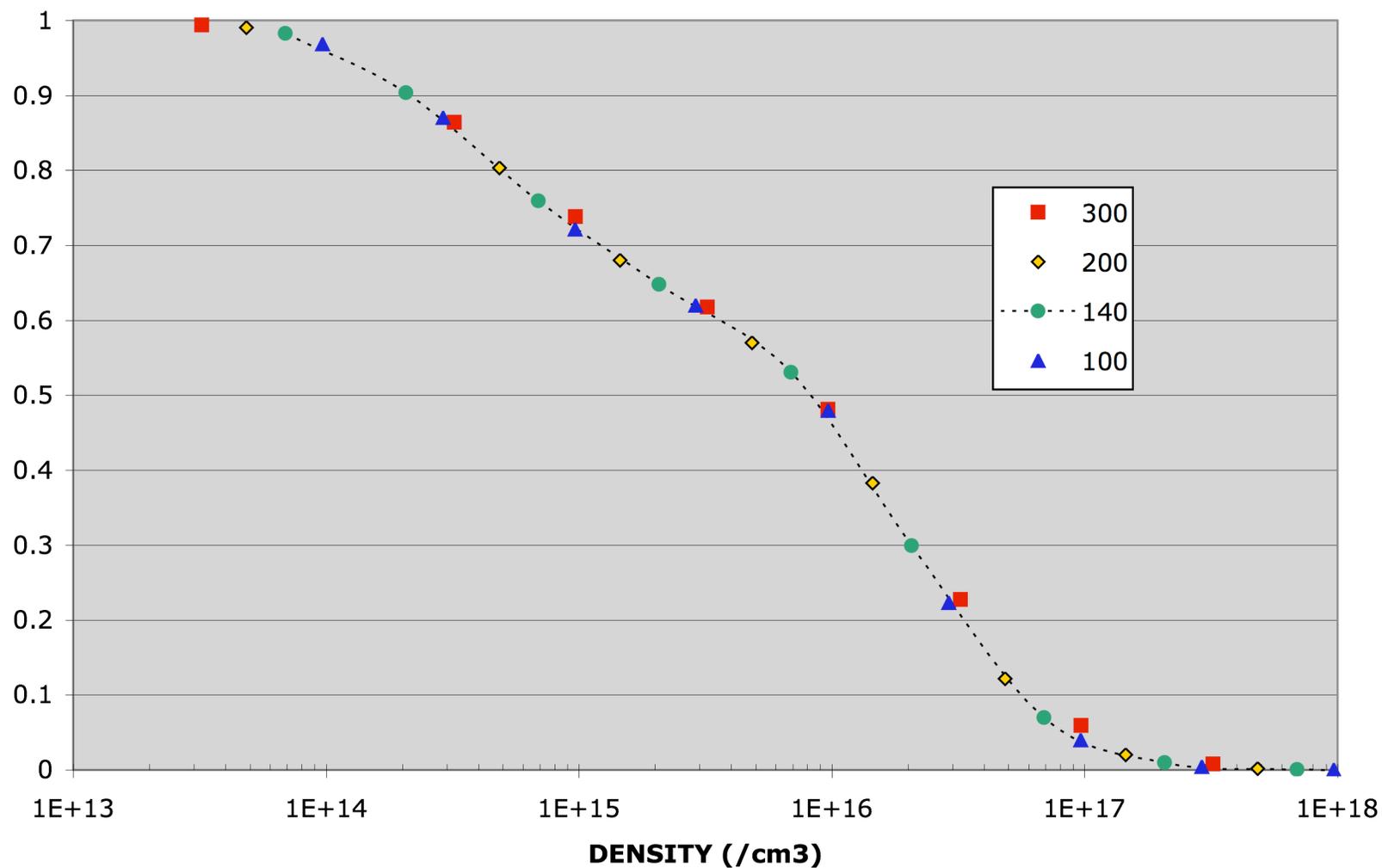


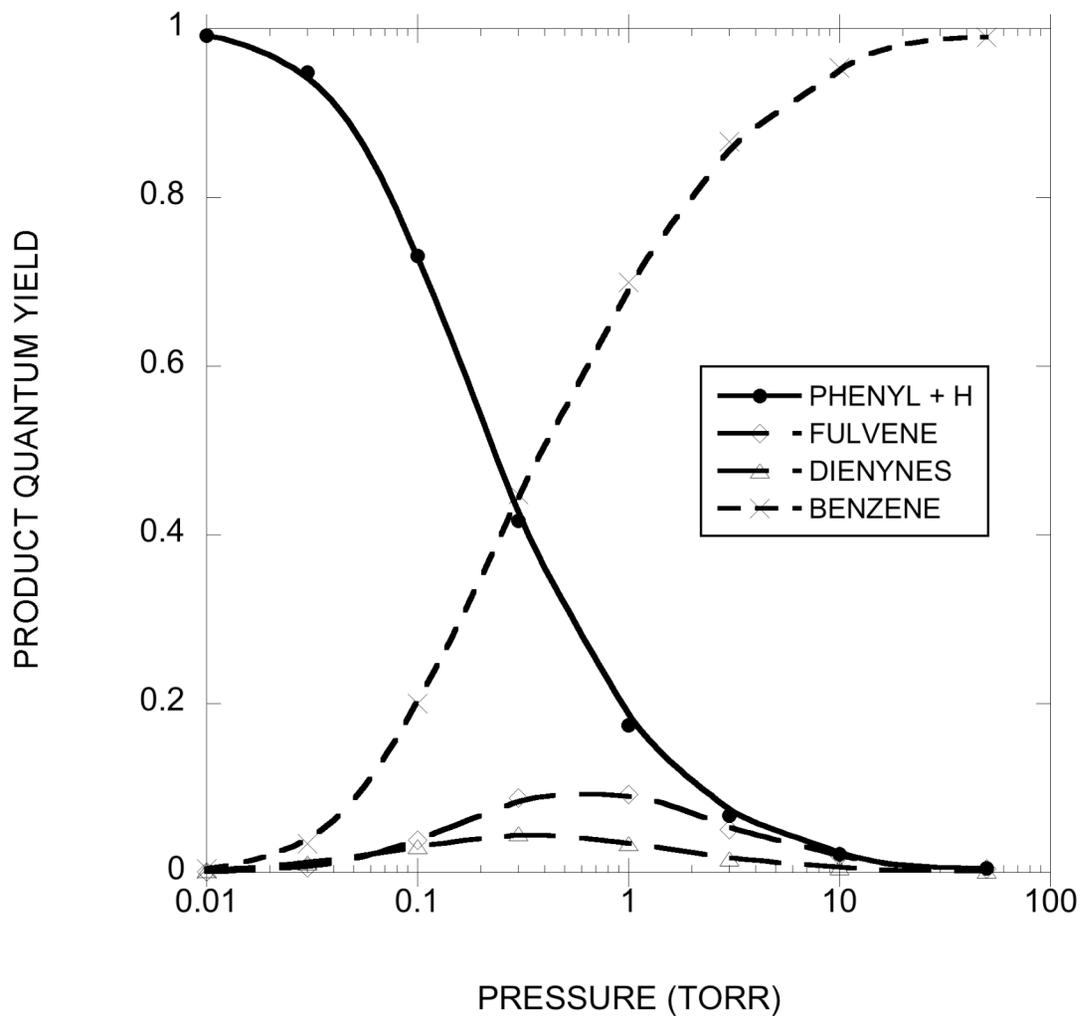
LINEAR PRODUCTS DOMINATE ABOVE 1 MBAR PRESSURE
AROMATICS AT LOWER PRESSURE, DOMINATE BELOW 0.1 TORR

PROPARGYL RECOMBINATION AT 140 K



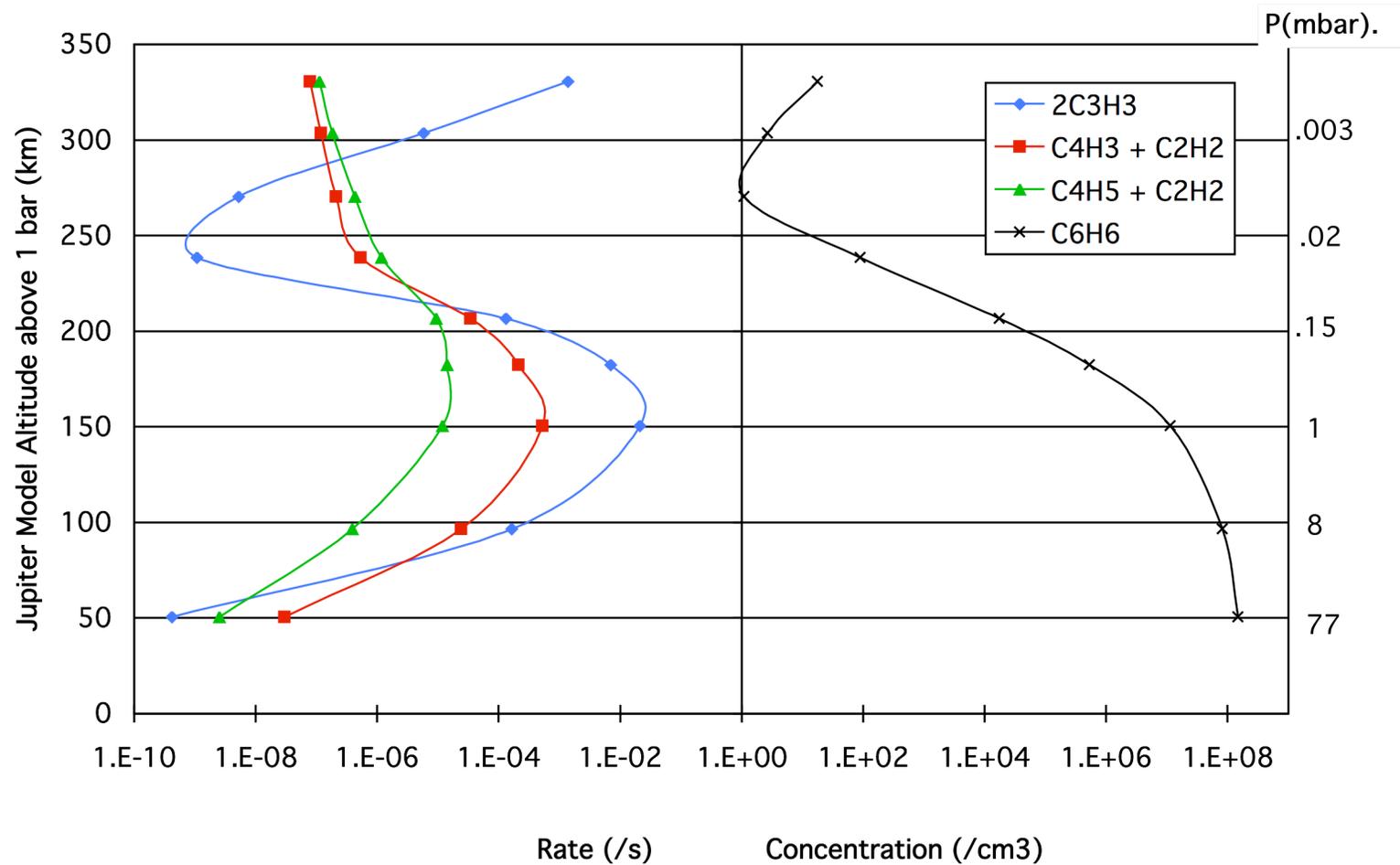
Calculated Yield of Benzene and Phenyl from Propargyl Recombination versus Density at the Temperatures Shown





The same master equation setup can calculate pressure dependent photolysis yields, assuming rapid internal conversion of the photoexcitation energy.

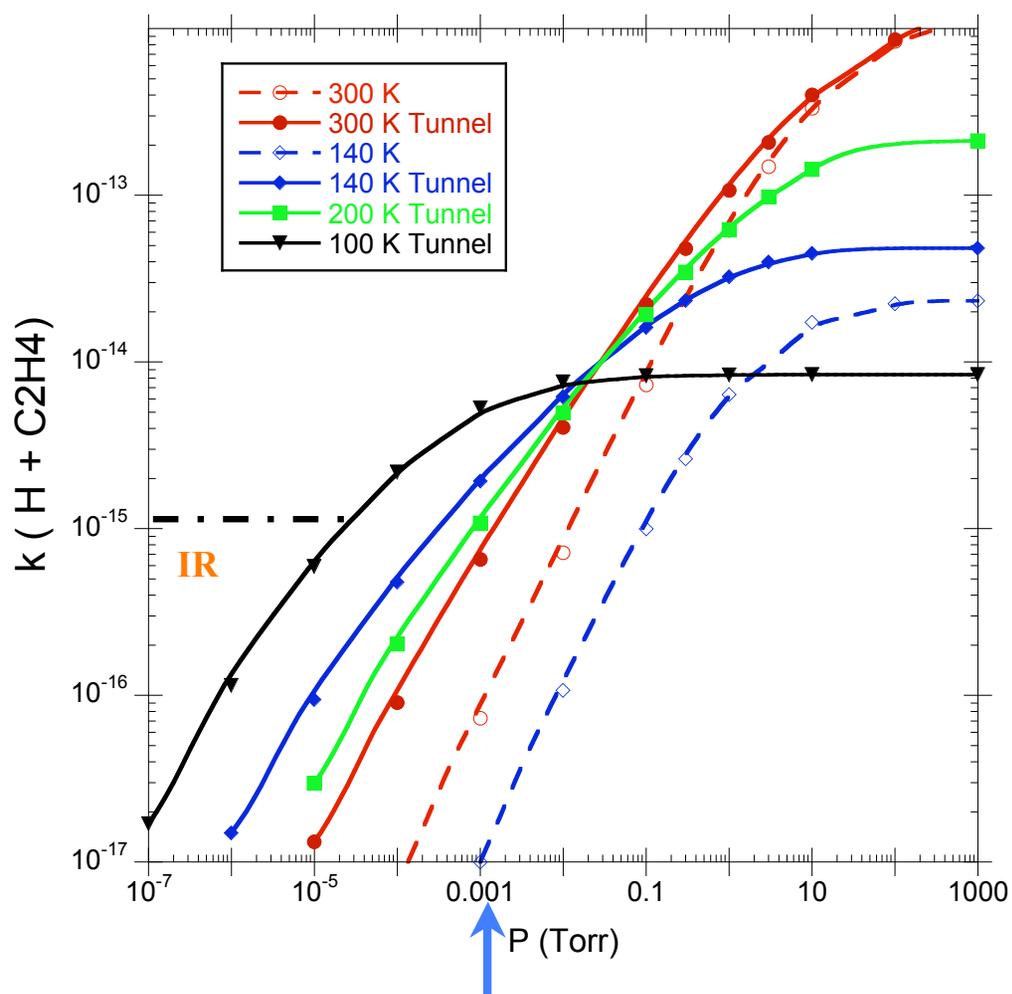
Calculated pressure dependence of benzene photolysis product yields at 191 nm (150 kcal/mole) and 165 K. Little net aromatic loss is predicted.



Benzene/phenyl formation rates for 3 reactions (left) and benzene concentration profile (right) for Jupiter's atmosphere using species profiles from the 2005 model of Moses et al. Our new low T,P rate constants for 3 alternative mechanisms show propargyl self-reaction is likely source for planetary benzene. (Left scale is altitude above 1 bar level, in km.)

H addition and recombination reactions prominent in important chemistry.
 Ethyl, Vinyl, Allyl Formation by H Addition to Ethylene, Acetylene, Allene

Ex.: Reaction $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$ has 2.4 kcal/mole barrier, but tunneling occurs!
 Effects at low pressure from tunneling and radiative stabilization.



$$k_{\infty}(140\text{K}) = 5.1 \times 10^{-14}$$

$$\kappa(\text{tunnel}) = 4$$

Note huge low T effects on k_0 (200x). Tunneling removes the E_0 barrier from $\text{A} + \text{B} = \text{AB}^*$ equilibrium. (Knyazev & Slagle 96 C_2H_3)

IR radiative stabilization sets a floor on low T k .

At very low pressures, IR radiative stabilization will place a lower limit on these rate constants. At low T and E, this is competitive with decomposition of the activated complex, k_2 . Use the Multiwell code to compute density of states with the IR active mode excluded; the ratio can be used to derive populations of emitting modes vs. energy. Using IR band strengths, related to lifetimes, $k_{\text{rad}}(E)$ is calculated, or $k_{\text{rad}}(E_{\langle kT \rangle})$ estimated. (Barker, Dunbar)

$$k(\text{rad}) = g\rho(N-1, E-h\nu)/\rho(N, E)/\tau(\text{rad}), \quad E = E_0 + E(kT)$$

$$k(\text{rad}) = \sum x g\rho(N-x, E-xh\nu)/\rho(N, E)/\tau(\text{rad}).$$

Some results for H addition products:

$$\text{C}_2\text{H}_5: k(0) \sim k_0[M] @ 10^{-5} \text{ torr } 100\text{K}, \sim 10^{-15} \text{ cm}^3/\text{s}$$

$$\text{C}_3\text{H}_5: \text{ at } 100\text{-}140\text{K}, k(0) \sim k_0[M] @ 10^{-5} \text{ t } \text{ and } k \sim k_\infty$$

$$\text{H} + \text{C}_3\text{H}_5 \rightarrow \text{C}_3\text{H}_6 + \text{IR} : k(0) \sim 7 \times 10^{-11} \text{ at } 140\text{K} \sim k_\infty/3$$

Fast rates for stable molecules at low T may overcome the P falloff

Lowest energy channel only

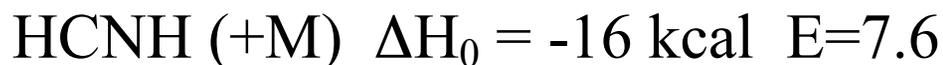
Another example, interconversion of 2 observed nitriles:

H + **HCCCN** → C₂H₂CN Experimental barrier of 1 kcal/mole, poor quantum predictions, thus uncertain tunnel frequency. (used est. 670i)

$$k_{\infty} \sim 1.1 \times 10^{-12} e^{-500/T}; k_0 \sim 5.6 \times 10^{-26} (T/300)^{-1.34}; F_c = 0.6$$

H + C₂H₂CN → **CH₂CHCN** simple barrierless recombination

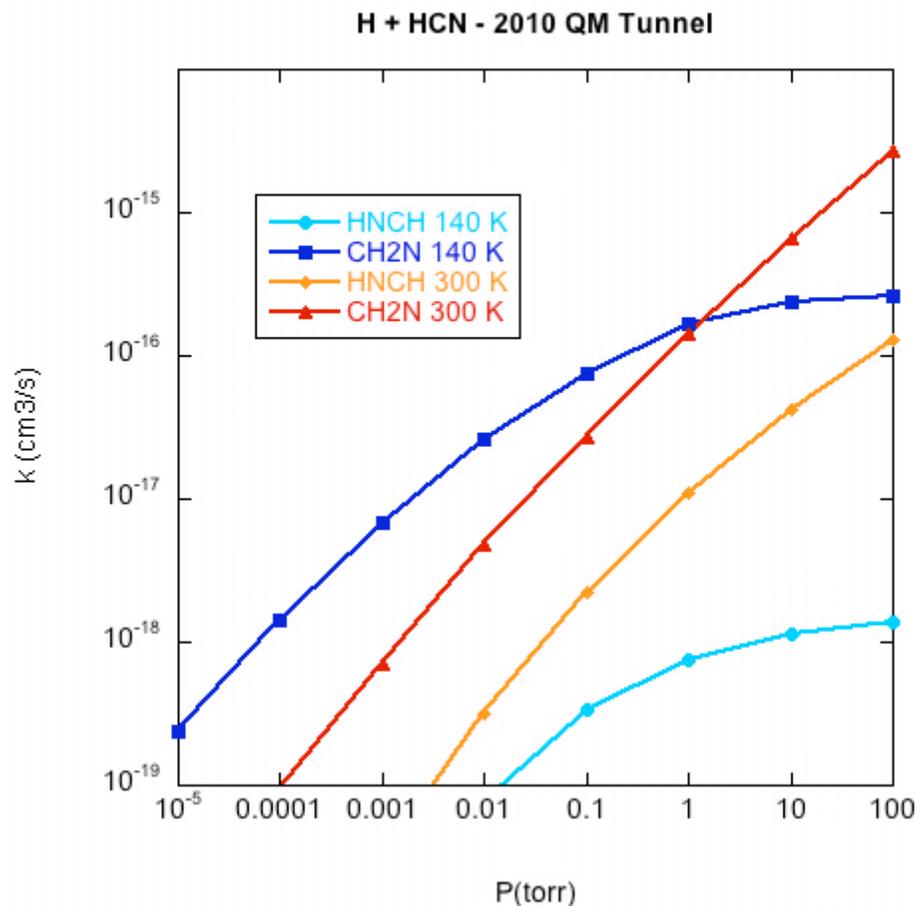
$$\text{est. } k_{\infty} \sim 2 \times 10^{-11}, \text{ calc. } k_0 = 5.0 \times 10^{-24} (T/300)^{-1.39}$$



Our DFT-computed (6-311++G(2d,2p)/MPW1K) addition barrier is high (consistent with others) giving slow calculated rate constants –

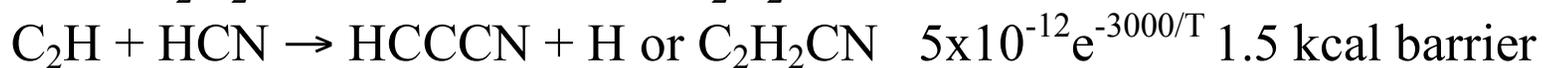
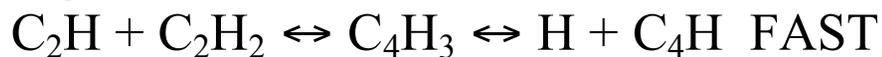
$$k_{\infty} = 2.43 \times 10^{-33} T^{7.964} \text{ and } k_0 = 2.57 \times 10^{-9} T^{-8.635} e^{-1048/T}$$

→ Almost no HCNH can be made by this H addition route. This species has been proposed to initiate HCN polymerization, (Wilson & Atreya 03) but it is difficult to locate feasible low T routes to high N/C nitriles.



Master equation rate constants for $\text{H} + \text{HCN} \rightarrow \text{CH}_2\text{N}, \text{HCNH}$ using the theoretical 4.6, 7.6 kcal/mole barrier heights and $764i \text{ cm}^{-1}$ tunneling frequency. (6-311++G(2d,2p) mpw1k) Large tunnel effect greatly increases the low P rates at low T.

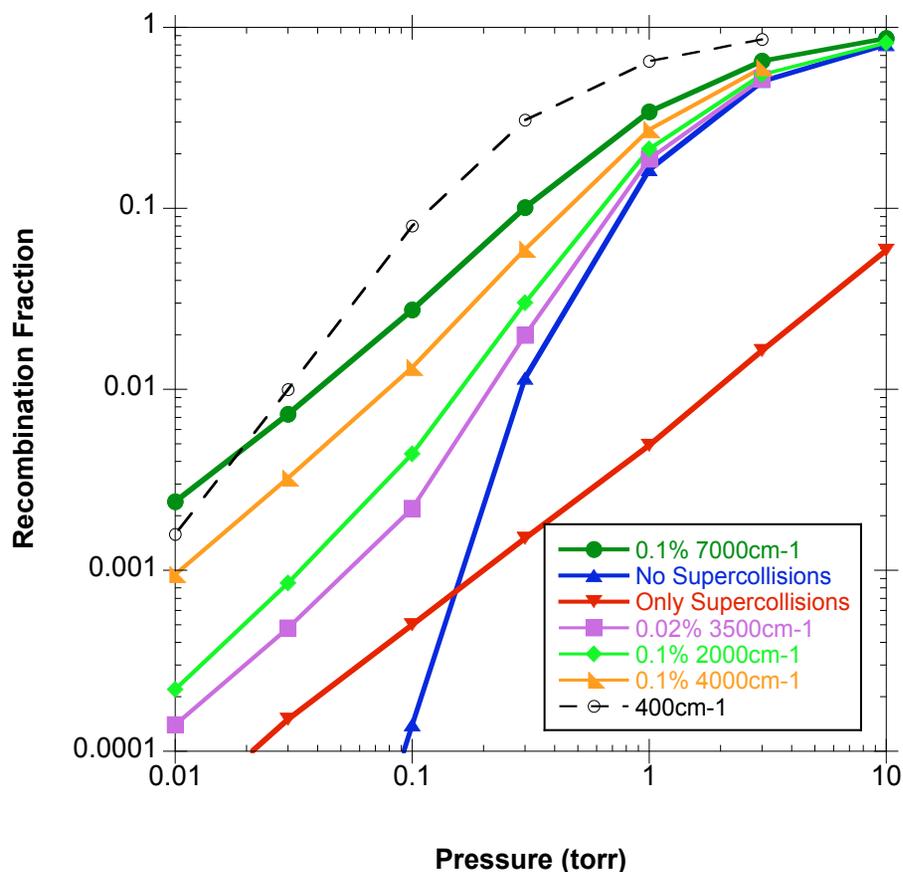
significant known addition routes for chain growth:



CN + HCCCN fast; but CN + NCCN has a 3-4 kcal barrier

-- hard adding to HCN at low T

There is evidence in the literature for a small fraction of collisions removing large amounts of energy. (see Oref, Barker, Mullin, Liu) This can have a large effect on higher energy channel recombination reactions at low pressure. Non-linear and higher order pressure dependences and abnormal falloff curves can occur.



Recombination / Chemical Activation :

Propane



Effect of Minority Supercollisions on Higher Energy Channel Recombination

Calculated pressure falloff (k/k_∞) for $\text{H} + i\text{C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_8$ at 150 K for various collisional energy transfer assumptions. ($2000 \text{ cm}^{-1} = 5.7 \text{ kcal}$)

- Dashed green line shows effect of increasing the ΔE parameter from 105 to 400 cm^{-1} .
- Various colored lines show the effect of varying the fraction and ΔE of supercollisions.
- The lowest red line allows only supercollisions, at 0.1% of the gas kinetic rate.
- Low pressure exponents of 1.5-4 without supercollisions; odd falloff shapes.



A

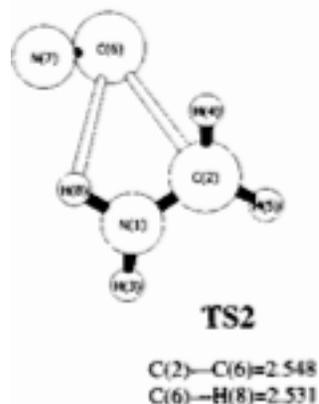
B

$$\Delta H_o(A) = -69.1(76.4) \text{ kcal}$$

$$\Delta E_o(B) = -37.5$$

$$\Delta E_o(A \rightarrow B) = -4.4$$

- This reaction converts a nitrile to an amine, NH_x to HCN.
- The amino-acetonitrile intermediate that might be stabilized at high pressure is (via hydrolysis) a precursor to amino acid glycine.
- The transition state for B involves a rearrangement with an **energy barrier**.
- 6-311++G(2d,2p)/mpw1k calculations used for energies and transition state B parameters. (see also Basiuk JPC A 105, 4252)

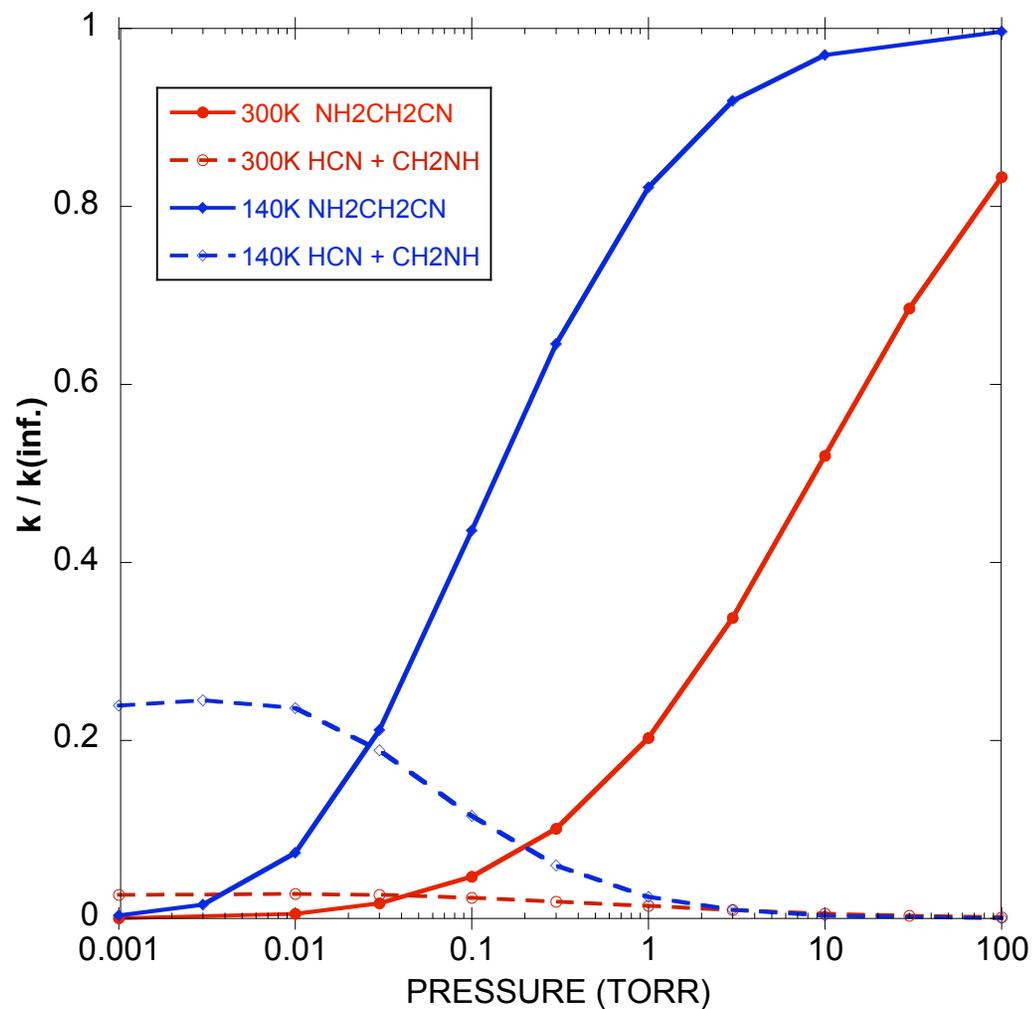


$$k_\infty(A) = 6.7 \times 10^{-12} T^{0.5} \text{ cm}^3/\text{molec/s}$$

$$k_o(A) = 10^{-22} T^{-1.93} e^{-105/T} \text{ cm}^6/\text{molec}^2/\text{s}; Fc = 1.0$$

$$k_o(A \rightarrow B) = 0.106 T^{-4.08} e^{-321/T} \text{ cm}^3/\text{molec/s}$$

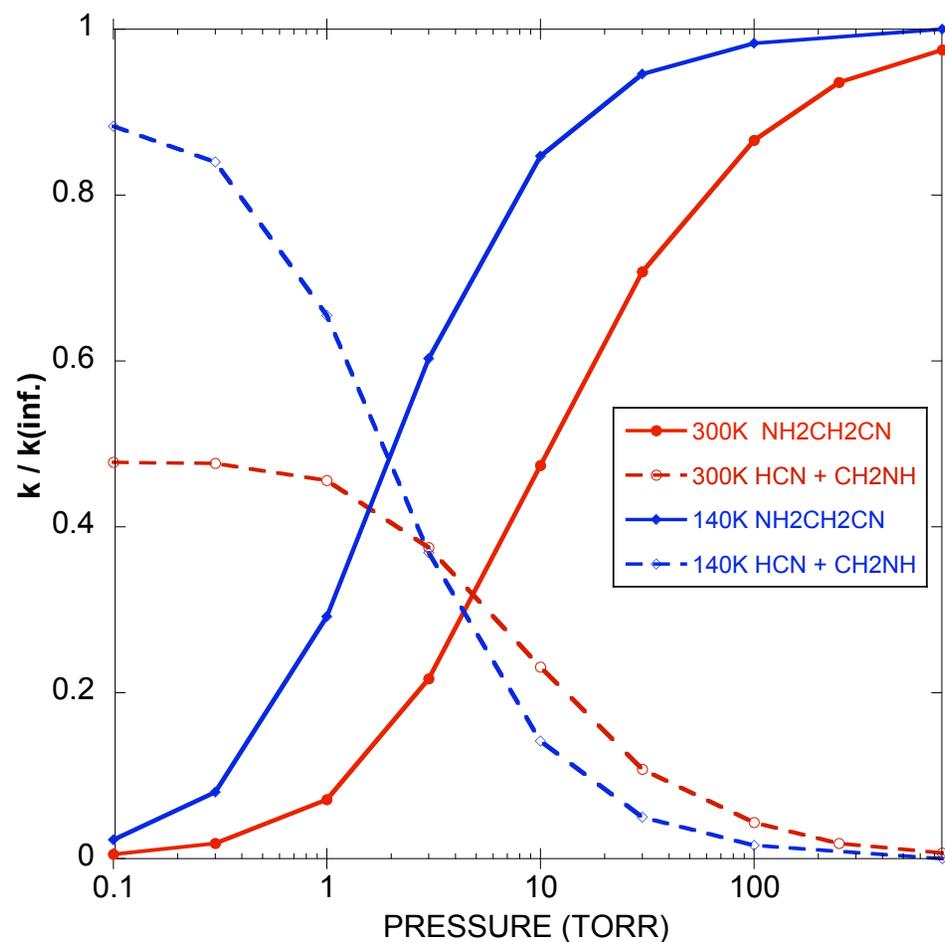
$$k(A \rightarrow B) = k_o(A \rightarrow B) \times (1 - k(A)/k_\infty(A))$$



Fraction of the high pressure limit recombination rate constant going to each specified product channel for the $\text{NH}_2 + \text{CH}_2\text{CN}$ reaction at 2 temperatures, vs. pressure.

Some of the excited complex falls back apart to reactants at low pressure.

Falloff depends on uncertain difference in energy barriers, and thermodynamics. Above used a calculated rearrangement barrier 4.4 kcal/mole below the entrance. Basiuk, and Xu & Wang computed lower TS(B) barriers relative to $\text{NH}_2\text{CH}_2\text{CN}$. This shifts falloff pressures 10x higher and increases the chemical activation yield, as shown for $\Delta\Delta E_0 = -16$ kcal/mole:



CHEMISTRY FOR AEROSOLS & HAZE:

Making large and complex organic polymers in reducing planetary atmospheres and predicting haze compositions can be divided into gas phase, condensation, and heterogeneous processes:

- A. Reactions forming larger molecules occur in the gas phase photochemistry.
- B. Chemical synthesis and transport produce concentrations of species above their vapor pressures, leading to condensation.
- C. Reactions and photochemistry continue in the aerosols, including gas-surface processes, producing larger polymeric species.

Quantum and rate theory methods can be applied to estimate likely reactions and rate constants, for the gas phase (A) part.

Low T vapor pressures fall quite dramatically with molecular size, so it is possible to select an upper limit in each category for consideration of the gas-phase precursor chemistry – 3 rings or 10 C+N atoms.

Aromatic Growth Mechanisms

A) Consider addition steps with low barriers from soot literature

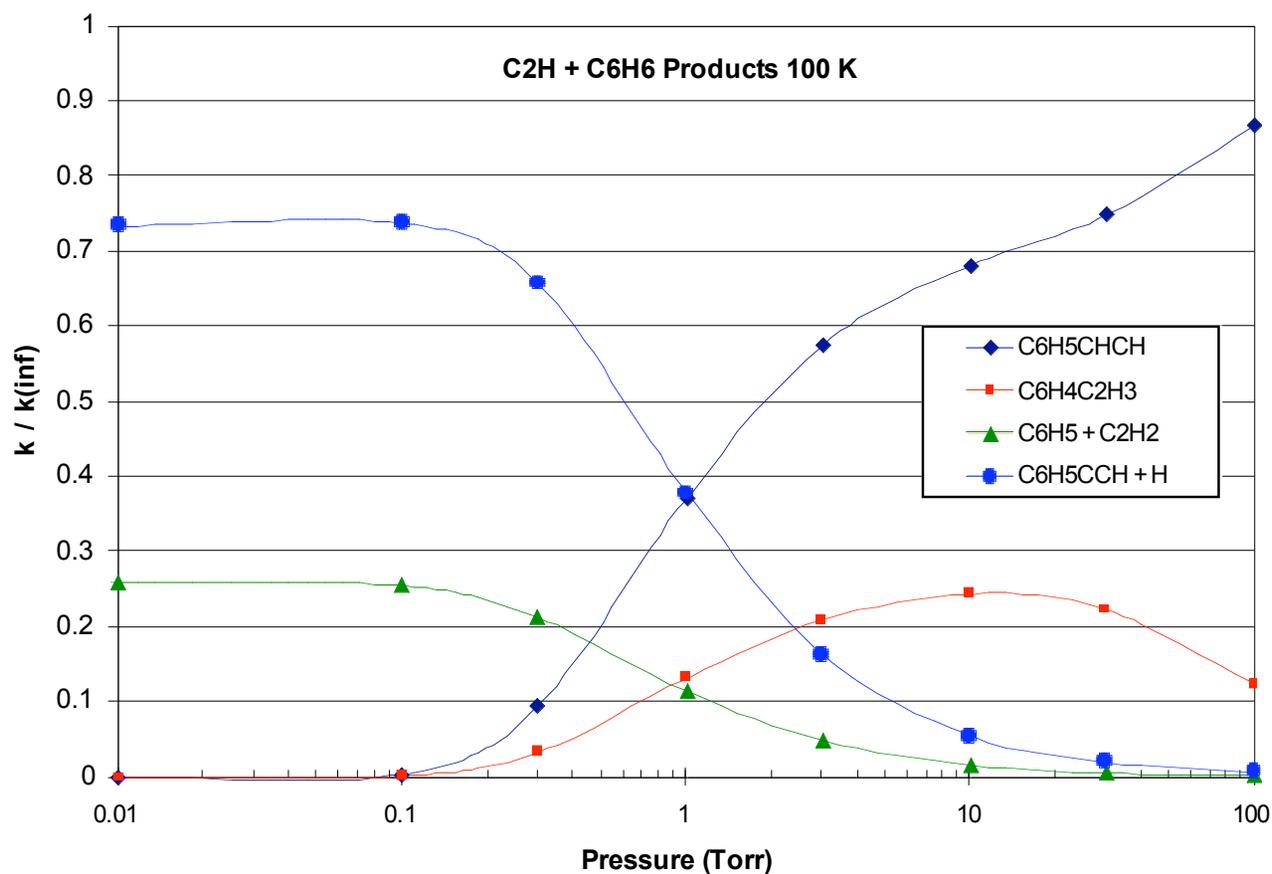
- Sequential C_2H_x additions (w. H loss and rearrangements) will form naphthalene from benzene.

- $cyC_6H_5 + C_2H_2$ barrier ~ 4 kcal/mole, slows rates greatly at low T
So rates computed with the Wang & Frenklach mechanism are slow.

- Start with barrierless $C_2H\cdot + cyC_6H_6$,
or recombination $cyC_6H_5 + C_2H_3 \rightarrow cyC_6H_5C_2H_3$

Calculations for $C_2H + C_6H_6$ using abridged surface parameters of Tokmakov & Lin (JACS 2003 125:11397)

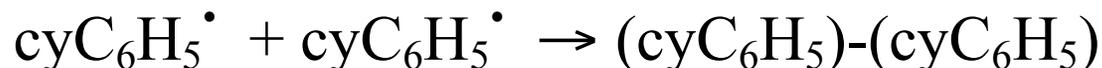
$C_2H + C_6H_6 \leftrightarrow C_6H_5CHCH^*$ (-62.4)	$C_6H_5CHCH^* \rightarrow C_6H_5CCH + H$ (-30.6)
$C_6H_5CHCH^* \leftrightarrow C_6H_5CCH_2^*$ (-69.6)	$C_6H_5CCH_2^* \rightarrow C_6H_5CCH + H$ (-30.6)
$C_6H_5CHCH^* \leftrightarrow C_6H_4C_2H_3^*$ (-61.2)	$C_6H_5CHCH^* \rightarrow C_6H_5 + C_2H_2$ (-21.9)



B) Some radical-radical pathways to larger aromatics also merit consideration, pathways less important for high T combustion / pyrolysis / soot chemistry

For example:

1. Form biphenyl from two phenyl radicals (McKay)



Lose para H by abstraction or photolysis \rightarrow $(\text{cyC}_6\text{H}_5)\text{-(cyC}_6\text{H}_4^\bullet)$

Recombine with a CH_3 radical \rightarrow $(\text{cyC}_6\text{H}_5)\text{-(cyC}_6\text{H}_4\text{CH}_3)$

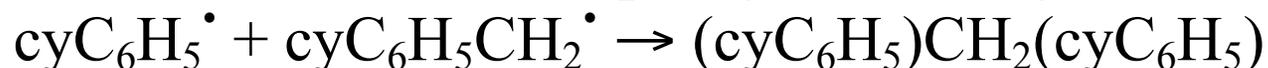
Abstract the weak benzylic H \rightarrow $(\text{cyC}_6\text{H}_5)\text{-(cyC}_6\text{H}_4\text{CH}_2^\bullet)$

Close center 5 member ring and lose other para H, forming fluorene

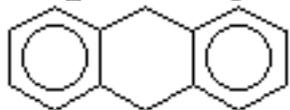


(adding a C_2H_x radical instead leads to phenanthrene)

2. Fast recombination of phenyl and benzyl radicals



Repeating the same steps above yields (9,10) dihydroanthracene



(loss of 2 H then would make anthracene)

Conclusions –

With guidance from literature and quantum calculations, master equation computations can provide adequate rate parameters for cold low pressure Jovian planet reducing atmospheric chemistry and photolysis. Transport and observational uncertainties mitigate the need for high accuracy.

Interesting phenomena may play large roles under such marginal conditions: tunneling, IR radiative stabilization, low probability super-stabilizing collisions in chemical activation systems, and large k_0 values. Hard to address experimentally.

Refinements from T dependence of energy transfer ΔE , and treatments of angular momentum conservation remain to be considered.