

# The Construction of a Gas-Phase Chemical Network for Dense Regions



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# Gaseous interstellar molecules (>150)

N=2		N=3		N=4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
H <sub>2</sub>	AlCl	CH <sub>2</sub>	C <sub>2</sub> S	NH <sub>3</sub>	CH <sub>4</sub>	CH <sub>3</sub> OH	CH <sub>3</sub> NH <sub>2</sub>	HCOOCH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> CO
CH	PN	H <sub>2</sub> S	OCS	H <sub>2</sub> CO	SiH <sub>4</sub>	CH <sub>3</sub> SH	CH <sub>3</sub> CCH	CH <sub>3</sub> C <sub>2</sub> CN	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> C <sub>4</sub> CN
NH	SiN	NH <sub>2</sub>	CCP	H <sub>2</sub> CS	CH <sub>2</sub> NH	C <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> CHO	HC <sub>6</sub> H	C <sub>2</sub> H <sub>5</sub> CN	CH <sub>3</sub> CH <sub>2</sub> CHO
OH	SiO	H <sub>2</sub> O	SiNC	H <sub>2</sub> CN	C <sub>5</sub>	H <sub>2</sub> C <sub>4</sub>	c-CH <sub>2</sub> OCH <sub>2</sub>	C <sub>7</sub> H	CH <sub>3</sub> C <sub>4</sub> H	(CH <sub>2</sub> OH) <sub>2</sub>
O <sub>2</sub> (?)	SiS	HNO	NaCN	<i>l</i> -C <sub>3</sub> H	<i>l</i> -C <sub>3</sub> H <sub>2</sub>	CH <sub>3</sub> CN	CH <sub>2</sub> CHCN	HOCH <sub>2</sub> CHO	C <sub>8</sub> H	
HF	PO	C <sub>2</sub> H	SO <sub>2</sub>	c-C <sub>3</sub> H	c-C <sub>3</sub> H <sub>2</sub>	CH <sub>3</sub> NC	HC <sub>4</sub> CN	CH <sub>3</sub> COOH	HC <sub>6</sub> CN	
C <sub>2</sub>	SH	HCN	N <sub>2</sub> O	HCCH	H <sub>2</sub> CCN	NH <sub>2</sub> CHO	C <sub>6</sub> H	H <sub>2</sub> CCCHCN	CH <sub>3</sub> CONH <sub>2</sub>	N = 11
CN	AlF	HNC	SiCN	HNCO	H <sub>2</sub> NCN	CH <sub>2</sub> CNH	H <sub>2</sub> CCHOH	H <sub>2</sub> C <sub>6</sub>	CH <sub>2</sub> CHCH <sub>3</sub>	HC <sub>8</sub> CN
CO	FeO	HCO		HNCS	CH <sub>2</sub> CO	C <sub>5</sub> H		CH <sub>2</sub> CHCHO		CH <sub>3</sub> C <sub>6</sub> H
CS	SiC	c-SiC <sub>2</sub>		HCCN	HCOOH	C <sub>5</sub> N		C <sub>2</sub> H <sub>6</sub>		
CP		MgCN		C <sub>2</sub> CN	C <sub>4</sub> H	HC <sub>4</sub> N		NH <sub>2</sub> CH <sub>2</sub> CN		
NO		MgNC		C <sub>3</sub> O	HC <sub>2</sub> CN	C <sub>5</sub> S(?)				N = 12
NS		AlNC	H <sub>3</sub> <sup>+</sup>	C <sub>3</sub> S	HC <sub>2</sub> NC	HC <sub>4</sub> H				C <sub>6</sub> H <sub>6</sub>
SO		HCP	HCO <sup>+</sup>	c-SiC <sub>3</sub>	C <sub>4</sub> Si					
HCl	CH <sup>+</sup>	C <sub>3</sub>	HOC <sup>+</sup>	C <sub>3</sub> N <sup>-</sup>	HNCCC	HC <sub>2</sub> CHO				
NaCl	CO <sup>+</sup>	C <sub>2</sub> O	N <sub>2</sub> H <sup>+</sup>	H <sub>3</sub> O <sup>+</sup>	CNCHO	c-C <sub>3</sub> H <sub>2</sub> O				N = 13
KCl	SO <sup>+</sup>	CO <sub>2</sub>	HCS <sup>+</sup>	HCNH <sup>+</sup>	H <sub>2</sub> COH <sup>+</sup>					HC <sub>10</sub> CN
N <sub>2</sub> (?)	CF <sup>+</sup>		HCNO	HOCO <sup>+</sup>	C <sub>4</sub> H <sup>-</sup>	HC <sub>3</sub> NH <sup>+</sup>	C <sub>6</sub> H <sup>-</sup>		C <sub>8</sub> H <sup>-</sup>	

# Gaseous Molecules - 1972

- H<sub>2</sub>, CH, CH<sup>+</sup>, CN, OH, CO, SiO, CS
  - H<sub>2</sub>O, H<sub>2</sub>S, HCO<sup>+</sup>, OCS
  - NH<sub>3</sub>, H<sub>2</sub>CO, HNCO
  - HC<sub>3</sub>N, HCOOH
  - CH<sub>3</sub>OH, CH<sub>3</sub>CN, NH<sub>2</sub>CHO
- 
- All dense clouds thought to be similar in their coldness; Sgr B2 most common source

# Considerations

- 1. Need for kinetics rather than thermodynamics?
- 2. Likely range of physical conditions (cold cloud, fluorescent lamp?)
- 2. Elements and abundances (an interstellar cloud? Our atmosphere?)
- 3. Steady-state or time-dependent (importance of initial concentrations)
- 4. Dominant processes
- 5. Historical: what is already known
- 6. Sequential: improvements & extensions based on new laboratory and theoretical work.
- 7. Experimental Collaborators

# In the beginning (Herbst & Klemperer 1973):

- Cold dense cloud (temperature “low”):
  - Non-thermodynamic system
  - Reactions must be exothermic and nearly barrierless
  - Existence of cosmic rays  $\rightarrow$  ions and ion-molecule reactions ( $\zeta_{\text{H}} = 10^{-15} - 10^{-17} \text{ s}^{-1}$ ) (Solomon & Werner 1971)
  - Dominant elements H and He  $\rightarrow$  ionization of H, H<sub>2</sub>, He most important
  - H<sub>2</sub> assumed to be dominant form of hydrogen based on prior work of Salpeter and colleagues
  - Steady-state then estimated to be reached quickly (**actually too quickly**)

# Efficient Low T Gas-Phase Reactions

1. Ion-molecule reactions
2. Radiative association reactions
3. Dissociative recombination reactions
4. Radical-radical reactions
5. Radical-stable reactions (later)
6. Photodestruction (diffuse gas)

$$E_a = 0$$

Exothermic

# H<sub>2</sub> Formation

- If necessary, assume that every H atom that hits and sticks to a cold grain leaves after reacting with another H atom (Jura).
- A pseudo-gas-phase rate law can then be obtained by using the well-known gas-to dust ratio:
- $d[\text{H}_2]/dt = k[\text{H}]n$ , where  $k$  is the velocity of H multiplied by the grain cross section multiplied by the dust-to-gas number ratio.

# Primary Ions



Elemental abundances: C, O, N =  $10^{-4}$ ; C < O



Primary ions:  $\text{H}_3^+$ ,  $\text{H}^+$ ,  $\text{He}^+$



## SECONDARY IONS & NEUTRALS



Similar story for OH, H<sub>2</sub>O (guessed branching fraction; later phase space theory, later experiments)

# Radical-Atom Processes

- $C + OH \rightarrow CO + H$
- $N + OH \rightarrow NO + H$
- $N + NO \rightarrow N_2 + O$
- $O + OH \rightarrow O_2 + H$
- $N + CH \rightarrow CN + H$

More secondary diatomics

# More Ions

- $\text{He}^+ + \text{CO} \rightarrow \text{C}^+ + \text{O} + \text{He}$
- $\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2$  prediction
- $\text{H}_3^+ + \text{N}_2 \rightarrow \text{HN}_2^+ + \text{H}_2$
- $\text{He}^+ + \text{N}_2 \rightarrow \text{N}^+ + \text{N} + \text{He}$
- $\text{C}^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2^+ + \text{H}_2, \text{C}_2\text{H}_3^+ +$   
 $\text{H}^{**}$

# Ammonia

- $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$  (slightly endothermic)
- Requires spin-orbit excitation of  $\text{N}^+$  or ortho- $\text{H}_2$  \*\*
- $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$  unusual temperature dependence \*\*
- $\text{NH}_4^+ + e \rightarrow \text{NH}_3 + \text{H}$  (est. 90%)

# Review: Chemical Formation and Destruction in HK

- **Ions**
- **Formation:**  $\zeta$ , ion-molecule reactions
- **Destruction:** dissociative recombination, reactions with  $H_2$  and atoms (C,O)
- **Neutrals**
- **Formation:** dissociative recombination and radical-neutral atom
- **Destruction:** ion-molecule reactions with 10 major ions
- **Radical destruction:** neutral reactions with atoms

# Cosmic Ray Photons

- Additional destruction step (Prasad & Tarafdar 1983)
- $e^* + H_2 \rightarrow H_2^* \rightarrow H_2 + \text{photon}$
- Leads to radiation field  $10^{-4}$  of unshielded interstellar UV field
- Rates written as  $a\zeta$ , with  $a \gg 1$

# Ion-Polar Reactions

- Herbst & Leung 1986 used the **locked-dipole approximation** for linear neutrals (assuming rotational relaxation) and an approximation to the **trajectory-scaling model** of non-linear neutrals. In both cases, large dipole approximations were used and only the T-dependent term was kept. ( $k$  prop. to  $T^{-1/2}$ )

# More Radiative Association Reactions

- $C^+ + H_2 \rightarrow CH_2^+$  (on to  $CH_5^+$ ) 1973
- $CH_3^+$  + polyatomics; e.g.
- $CH_3^+ + HCN \rightarrow CH_3NCH^+$  1980
- and later
- $C + H_2 \rightarrow CH_2$  2004?
- $CH + H_2 \rightarrow CH_3$  1997
- $C + C_3 \rightarrow C_4$  2004



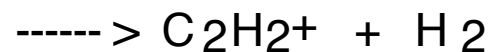
# Model History (pre-1990)

- 1973 Herbst & Klemperer: first dense cloud model (100 reactions) steady-state solution; paper tape
- 1980 Prasad & Huntress: first large models with many reactions and time-dependent solutions
- 1989 Herbst & Leung: first “complex” molecules included
- 1989: Millar, Bennett, Herbst: deuterium fractionation included in large models
- Important work of UMIST, Dalgarno, Langer, Roueff, Black, van Dishoeck, Smith, Tielens, Hollenbach and many others.....
- Ion-molecule studies by groups headed by David Smith, Wes Huntress, Eldon Ferguson, Bertrand Rowe, Dieter Gerlich, and others.....

## ORGANIC SYNTHESIS CONT. (HL 1989)

### SOME SYNTHETIC REACTION CLASSES:

#### A. CARBON INSERTION



#### B. CONDENSATION



#### C. ATOMIC INSERTION



#### D. LOSS OF HYDROGEN



#### E. NEUTRAL-NEUTRAL



# Carbon “Insertion” Route

- $C^+ + C_2H_2 \rightarrow C_3H^+ + H$
- $C_3H^+ + H_2 \rightarrow c-C_3H_3^+, H_2C_3H^+$
- $C^+ + C_3H_2 \rightarrow C_4H^+ + H$
- $C_4H^+ + H_2 \rightarrow C_4H_2^+ + H$
- $C_4H_2^+ + e \rightarrow C_4H + H$

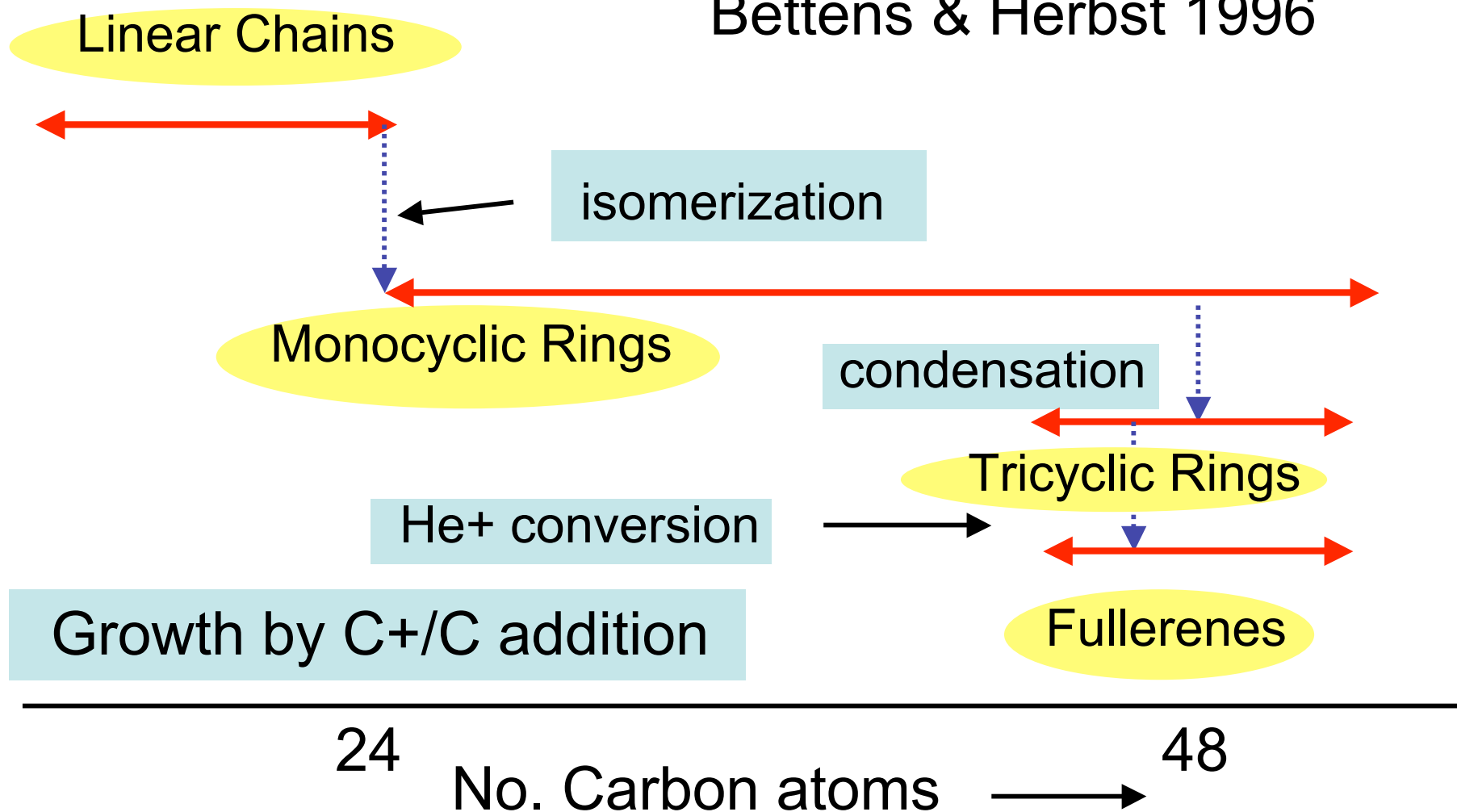
Unsaturated hydrocarbon products;  
tend towards linearity

# Radical-Neutral Reactions

- Started with the work of David Husain as discussed in Clary et al. 1994 for C atoms
- Most work (especially at low T) performed by Birmingham and Rennes groups since then although crossed-beam experiments have also proven to be useful.
- Herbst, Millar et al. 1994
- Bettens et al. “new neutral-neutral model” 1995
- Smith et al. osu.2003 (2004)
- NET RESULT: harder to produce large molecules if  $C < O$  (TMC-1 especially) unless models restricted to measured rates.

# EXTENSION TO FULLERENES

Bettens & Herbst 1996



# Addition of a New Molecule

- **Example:** CH<sub>2</sub>CNH (keteneimine)
- **Formation:** Most likely:
  - CH<sub>3</sub>CNH<sup>+</sup> + e → CH<sub>3</sub>CN + H;
  - CH<sub>3</sub>CN + H,
  - **CH<sub>2</sub>CNH** + H
- But how is protonated acetonitrile formed?
- CH<sub>3</sub><sup>+</sup> + HCN → C<sub>2</sub>H<sub>4</sub>N<sup>+</sup> (structure?)
- **Destruction:** reactions with ions; mainly but not completely by protonation, cosmic-ray photons

# Negative Ion Chemistry

- *Formation occurs by:*

- Radiative attachment (Herbst 1981)



- Dissociative attachment (Petrie & Herbst 1997)



(normally endothermic unless neutral an unusual species such as a carbene)

*Few experimental and detailed theoretical studies.....*

*Destruction occurs by associative detachment, mutual neutralization, and photodetachment as well as ion-molecule reactions, that lead to new ions.*

# Additions for Higher Temperatures

- Hot Cores 100-300 K
- Photon-dominated regions 100 – 1000 K (gas-phase)
- Shocks 1000-5000 K (gas-phase)
- Reactions with barriers and endothermic reactions turn on.
- $X + H_2 \rightarrow XH + H$  become important.
- Road to thermodynamics (stellar atmospheres) must include backwards reactions



# Rate Coefficient Estimation

- Guided extrapolation
- Ion-non-polar Langevin/ analogous systems
- Ion-polar trajectory scaling and locked dipole approaches (osu);  $T^{-1/2}$  law (Rate06)
- Dissociative recombination: estimation from experiments (H3+ + e most difficult)
- Radiative association: statistical estimate; three-body analogy (Sean Smith, Juergen, Jean-Christophe, Ian, Bates, Herbst)
- Attachment: statistical estimate (Herbst)
- Radical-neutral: ask Ian/ analogous systems/ two-transition-state model (see Klippenstein in Ian's new book)

# Product Estimation

- Exothermicity, spin conservation
- Similar reactions and classes (e.g. protonation, H-atom transfer)
- Calculations
- Ask experts (Ian, David Smith, Wolff Geppert)

# Current Gas-Phase Networks

Rate06\* [www.udfa.net](http://www.udfa.net) (every 5 years)

osu.2008\* [www.physics.ohio-state.edu/~eric/](http://www.physics.ohio-state.edu/~eric/) (maintained by Valentine)

Meudon <http://aristote.obspm.fr/MIS/>

Others: PAHs (Lepp & Dalgarno, Valentine), shocks (des Forêts), IRC+10216 (C-rich, joint UMIST-osu), thermodynamic equilibrium (Andrew Markwick-Kemper)

\* Anion extensions available upon request (similar results for cold clouds) Walsh et al.

# The Future

- Gas-grain networks
- Stochastic solutions
- Coupled with hydrodynamics
- Solved for cold cores, pre-stellar cores, hot cores, protoplanetary disks, PDR's XRDR's, diffuse clouds, IR dark clouds, external galaxies, early universe....
- Teams of investigators