Theoretical investigation of H$_2$CO and H$_3$COH formation in the interstellar medium

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Goals

• Goals of FORCOMS* theoretical chemistry part:
  
  – how reactions on dust grains contribute to the formation of key Complex Organic Molecules (COMs)
  
  – Using QC calculations with explicit water molecules (≠ solvent model calculations)
  
  – Gas phase reactions as benchmarks

*ANR FORCOMS (2009-2012) Formation of Complex Molecules in Space
Our Work is focused on modelling COM formation in Dense clouds
Very Low T
Successive hydrogenation of CO are supposed to lead to formaldehyde and methanol formation.
Why?

✧ Gas Phase reactions are hindered by energy barriers, tunneling has been invoked

✧ Experiments (Watanabe et al, Linnartz et al, Parent et al) observed the production of H\textsubscript{2}CO and subsequently H\textsubscript{3}COH when exposing CO ices to H atoms.

✧ The experiments also showed that the surface of Amorphous Solid Water (ASW), enhances the reaction, H (D) + CO → HCO (DCO). The origin of this enhancement due to ASW is not clear. ASW may modify the activation barriers and enhance the tunneling probability, and/or the adsorption energy of H atom.

✧ This is important to clarify as astrophysical models require the reaction rates and energetics associated with all of the reaction steps.
Why?
Overview of processes on grains

Formation of a mantle if T is low enough, mainly composed of water (+ CO, NH₃, CH₄, CH₃OH, H₂CO, ...)

Reaction:
Langmuir-Hinshelwood
Eley-Rideal
photodissociation

Desorption:
thermal desorption
photodesorption by UV rays
CR heating of the grain
release of chemical energy

Diffusion:
thermal hopping between potential wells separated by energy barriers $E_d$
(tunnel effect for H at low T)
Methodology

High level ab initio and DFT calculations performed with using various programs (Molpro, Gaussian, Turbomol...)

Optimization of the reactant and product (normal modes analysis).
Search for the transition state and intrinsic coordinate (IRC) curve of the PES.
Computation of the tunelling probabilities when possible using the Eckart or WKB* formalisms
Potential energy (hyper)surface

- 3N-6 dimensions ⇒ PES impossible to obtain if N > 3
- Extrema characterised by calculating 2\textsuperscript{nd} order energy derivatives (Hessian)
  - Theoretical harmonic frequencies
  - Vibrational Zero-point Energy (ZPE)
Intrinsic Reaction Coordinate (IRC)

= Mass-weighthed steepest descent minimum energy path connecting reactants and products through saddle point (transition state)

1-D potential
⇒ Calculation of tunnelling rates
- Eckart (3 points needed)
- WKB (IRC curve needed)
Results: gas phase

1\textsuperscript{st} Hydrogenation \hspace{1cm} 2\textsuperscript{nd} Hydrogenation \hspace{1cm} 3\textsuperscript{rd} Hydrogenation \hspace{1cm} 4\textsuperscript{th} Hydrogenation

\begin{itemize}
  \item \textbf{CO} \[ E_a \approx 32 \text{ kcal/mol} \]
  \item \textbf{HCO} \[ E_a \approx 5 \text{ kcal/mol} \]
  \item \textbf{COH} \[ E_a \approx 23 \text{ kcal/mol} \]
  \item \textbf{HCOH} \[ E_a \approx 29.7 \text{ kcal/mol} \]
  \item \textbf{H}_2\textbf{COH}
  \item \textbf{H}_3\textbf{COH}
\end{itemize}
H + CO → HCO benchmark

- Previous works:
  
  Barrier: 2.0 ± 0.4 kcal/mol (Exp.) → 3.5 ± 0.4 kcal/mol (Theor.)

  ![Graph](image)

  FIG. 2. Arrhenius plot, showing ln k vs 1/T (°K⁻¹), for the reaction H + CO → HCO. ● Average of two or more runs at a given temperature, ○ single run, and ◆ from Ref. 1.


Present work

- Up to (aug)-cc-pCVXZ, X=6
- MRCI+Q
- Core-valence effects
- Anharmonic frequencies
- CBS extrapolation(s) (4 expressions)
- Scalar relativistic effects (Douglas-Kroll-Hess)
- Spin-orbit: negligible
- Non-Born-Oppenheimer Correction: negligible
### Results

<table>
<thead>
<tr>
<th></th>
<th>cc-pVXZ</th>
<th>aug-cc-pVXZ</th>
<th>cc-pCVXZ</th>
<th>cc-pVXZ-DK</th>
<th>cc-pCVXZ-DK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HCO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Barrier</strong></td>
<td>3.93 ± 0.06</td>
<td>3.91 ± 0.08</td>
<td>4.46 ± 0.06</td>
<td>4.45 ± 0.06</td>
<td>4.54 ± 0.14</td>
</tr>
<tr>
<td><strong>Ergicity</strong></td>
<td>-13.97 ± 0.22</td>
<td>-13.97 ± 0.30</td>
<td>-13.80 ± 0.11</td>
<td>-13.93 ± 0.11</td>
<td>-13.36 ± 0.57</td>
</tr>
<tr>
<td><strong>Dissociation</strong></td>
<td>17.79 ± 0.18</td>
<td>17.77 ± 0.22</td>
<td>18.14 ± 0.09</td>
<td>17.20 ± 1.33</td>
<td>17.78 ± 0.43</td>
</tr>
</tbody>
</table>

- **Experimental activation energy:** \(2.0 \pm 0.4\) kcal mol\(^{-1}\)
- **Experimental ergicity:** \(-13.9 \pm 0.4\) kcal mol\(^{-1}\)

1 kcal/mol = 500K

**Need for a new experimental determination of the barrier**
## Failure of DFT!

(No ZPE)

<table>
<thead>
<tr>
<th>Method</th>
<th>Barrier Height</th>
<th>Dissociation barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid</td>
<td>-0.73—4.07</td>
<td>24.60—26.67</td>
</tr>
<tr>
<td>Hybrid Meta</td>
<td>-4.20—2.56</td>
<td>24.15—25.89</td>
</tr>
<tr>
<td>Pure or Meta</td>
<td>-7.56—2.15</td>
<td>23.45—26.36</td>
</tr>
</tbody>
</table>

This work

<table>
<thead>
<tr>
<th>Method</th>
<th>Barrier Height</th>
<th>Dissociation barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>0.71</td>
<td>26.00</td>
</tr>
<tr>
<td>B971</td>
<td>3.85</td>
<td>26.26</td>
</tr>
<tr>
<td>KMLYP</td>
<td>0.39</td>
<td>22.64</td>
</tr>
<tr>
<td>PBEPBE1</td>
<td>1.24</td>
<td>21.4</td>
</tr>
<tr>
<td>B2PLYP</td>
<td>2.59</td>
<td>24.10</td>
</tr>
<tr>
<td>BHandHLYP</td>
<td>1.74</td>
<td>20.09</td>
</tr>
<tr>
<td>BP86</td>
<td>0.01</td>
<td>23.03</td>
</tr>
<tr>
<td>KMLYP-mod</td>
<td>2.43</td>
<td>17.87</td>
</tr>
<tr>
<td>TPSSH</td>
<td>-1.86</td>
<td>26.54</td>
</tr>
<tr>
<td>B97D</td>
<td>3.86</td>
<td>29.55</td>
</tr>
<tr>
<td>M06</td>
<td>3.54</td>
<td>25.01</td>
</tr>
<tr>
<td>M06-HF</td>
<td>4.92</td>
<td>21.55</td>
</tr>
<tr>
<td>M06-L</td>
<td>4.06</td>
<td>27.36</td>
</tr>
<tr>
<td>M06-2X</td>
<td>3.67</td>
<td>23.11</td>
</tr>
</tbody>
</table>

Experimental activation energy: $2.0 \pm 0.4$ kcal mol$^{-1}$
Further hydrogenations

aug-cc-pVTZ/ MRCI+Q (Molpro) and MRMP2 (Gamess)
Technical problems: CASSCF, IRC
Influence of the environment

Example of atmospheric reactions, ice can reduce reaction barriers

Icy grain modeled by a small cluster of water molecules

After 1st proton transfer (PT):


Proton relay mechanism facilitates the reaction?
Examples of reactions

\[
\text{HNC} \rightarrow \text{HCN}
\]


\[
\text{I}_2\cdot2\text{H}_2\text{O}
\]

H$_2$O clusters

\[
\text{CO} \xrightarrow{H} \text{HCO} \xrightarrow{H} \text{H}_2\text{CO} \xrightarrow{H} \text{CH}_3\text{O} (\text{or} \text{CH}_2\text{OH}) \xrightarrow{H} \text{CH}_3\text{OH}.
\]

In presence of up to n=5 H$_2$O

- B97D/aug-cc-pVTZ/Gaussian09
  - Good agreement with multi-ref. results in gas phase for H+CO

- BUT : B97D does not predict easily some TS in gas phase!
  - Absence of TS in clusters is either physical or a deficiency of B97D

- WKB for tunneling
The H$_2$O’s are participating

TS-HCO-(H$_2$O)$_5$

IRC-H3CO (H$_2$O)$_5$ - TS
1st hydrogenation

No effect on the first barrier
2nd hydrogenation

Relative Enthalpy (0K) (kcal/mol)

- H+HCO
- cis-HCOH
  - -28.52
  - -34.73
  - -37.60
- TS1
  - -5.58
- trans-HCOH
  - -32.02
  - -37.11
  - -50.15
- TS2
  - -5.39
- H₂CO
  - -85.76
  - -82.40
  - -87.53
Isomerization of HCOH to H₂CO

The geometries of the transition states computed at the MP2 / aug-cc-pVTZ with N water molecules for N = 0,1,2,3.
t-HCOH $\rightarrow$ H$_2$CO isomerisation

The Activation Energy is significantly reduced when Water is allowed to participate within the reaction.

Peters et al. JPCA 115 8983 (2011)
HCOH → H₂CO isomerisation

Through Tunneling?

• In 2008 the first experimental study of HCOH appeared in Nature

• During the study Schreiner et al. observe that HCOH isomerises to H₂CO even at 11 K. Since the barrier is too high to be surmounted at the temperature of the experiment, 11K, the conclusion is H atom tunnelling is responsible.


Peters et al. JPCA 115 8983 (2011)
3rd hydrogenation

Relative Enthalpy (0K) (kcal/mol)

-40 -30 -20 -10 0 10 20

H+H₂CO
TS1
TS3
TS2
H+H₂CO
H₂CO
H₂COH

n=5
n=0
n=3
Summary

• Sequential hydrogenations of CO up to CH$_3$OH studied ab initio from gas phase to clusters of H$_2$O
  – Influence of environment on isomerisation rates

• When the size of the system increases, switch from multi-reference methods to DFT
  – Limitations of the method: DFT has to be calibrated with pure ab initio
  – No DFT method can describe even qualitatively all bond formation processes
Summary

• Sequential hydrogenations of CO up to CH$_3$OH studied ab initio from gas phase to clusters of H$_2$O
  – Influence of environment on isomerisation rates

• When the size of the system increases, switch from multi-reference methods to DFT
  – Limitations of the method: DFT has to be calibrated with pure ab initio
  – No DFT method can describe even qualitatively all bond formation processes
Recommended Network for Astrophysical models
Perspectives

• Other molecules / mixed CO-H₂O

• Other approaches
  – New functionals? (Long-Range corrected? Accounting for van der Waals interactions and H-bonding)
  – MP2 : very expensive
  – QM/MM?
  – Dynamical calculations (classical, semi-classical, quantum)
Perspectives

• Solving the interaction with a ‘icy’ environment

Modeling the interactions of trace gases and aerosols
Context: atmospheric chemistry
LABEX CAPPA (Chemical and Physical Properties of the Atmosphere)

Reactivity of Polycyclic Aromatic hydrocarbons Reactivity in Cryogenic Solids
Context: interstellar chemistry
ANR PARCS with J. Mascetti and A. Simon (see poster)
Thank you for your attention
Effects of a cluster toward heterogeneous chemistry

CO clusters: $(CO)_n$, $n=4$ and $6$

CO-H$_2$O cluster: CO-(H$_2$O)$_n$, $n=3$ and $5$
CO clusters: \((\text{CO})_n\), \(n=4\) and 6

Pure \((\text{CO})_4\) cluster

(a) \(\text{HCO(CO)}_3\) and (b) \(\text{COH(CO)}_3\)

RI-MP2/aug-cc-pVTZ calculations
CO clusters: \((\text{CO})_n\), \(n=4\) and \(6\)

1st hydrogenation

(a) \(\text{HCO(CO)}_5\) and (b) \(\text{COH(CO)}_5\)

Pure \((\text{CO})_6\) cluster

RI-MP2/aug-cc-pVTZ calculations
CO clusters: \((\text{CO})_n\), \(n=4\) and \(6\)

### Energetics

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E_a)</th>
<th>(E_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H} + 4\text{CO} \rightarrow \text{HCO} \cdot (\text{CO})_3)</td>
<td>-</td>
<td>-19.40</td>
</tr>
<tr>
<td>(\text{H} + 4\text{CO} \rightarrow \text{COH} \cdot (\text{CO})_3)</td>
<td>-</td>
<td>+22.20</td>
</tr>
<tr>
<td>(\text{H} + 6\text{CO} \rightarrow \text{HCO} \cdot (\text{CO})_5)</td>
<td>-</td>
<td>-17.44</td>
</tr>
<tr>
<td>(\text{H} + 6\text{CO} \rightarrow \text{COH} \cdot (\text{CO})_5)</td>
<td>-</td>
<td>+23.93</td>
</tr>
<tr>
<td>(\text{H} + \text{CO} \rightarrow \text{HCO})</td>
<td>5.20</td>
<td>-17.37</td>
</tr>
<tr>
<td>(\text{H} + \text{CO} \rightarrow \text{COH})</td>
<td>41.45</td>
<td>+27.82</td>
</tr>
</tbody>
</table>

→ Stabilization of HCO and COH by the cluster but still COH production is endothermic

Note: It was not possible to isolate the TS mostly because of the flat PES (weak CO-CO bonding)

Activation energies \((E_a)\), and energies of reaction \((E_r)\) for \(\text{H} + \text{CO}\) in the presence of 3 CO, 5 CO, and in the gas phase for reference. Values are given in kcal/mol.

RI-MP2/aug-cc-pVTZ calculations
Ab initio methods

\[ H\Psi = E\Psi \]

- **Monoconfigurational methods:**
  \[ \Psi = 1 \text{ Slater déterminant (}=\text{mono-ref}) \]
  - Hartree-Fock
  - MP2 (Perturbation)
  - « Coupled Cluster » : CCSD(T)
  - Valid if 1 Slater determinant is a good approximation of the « real » \( \Psi \)
  - Lack electronic correlation
  - « large » systems

- **Multiconfigurational methods:**
  \[ \Psi = \text{ Linear combination of Slater determinants (}=\text{multi-ref}) \]
  - CASSCF
  - MRCI
  - CASPT2
  - ... (continued)
  - Purely \textit{ab initio}
  - Electronic excited states
  - Very expensive \( \Rightarrow \) small molecules / gas phase

GDR EMIE-Octobre 2013
HF

- Goal: « chemical » accuracy \( \leq 1 \text{ kcal/mol} = 503.2 \text{ K} 
- Compromise size of the system/computational cost \( \geq n^4 \)
Density Functional Theory?

- Use electronic density $\rho(r)$ instead of wave function $\Psi$: $\rho(r)$ contains all properties of the molecule
- Theorem: $\rho(r) \Leftrightarrow H$ unique

+ Formally exact in principle
+ Includes electronic correlation for the price of a Hartree-Fock calculation
  → « very large » systems (only first principles method)

- Exact functional unknown: approximate DFT in practice
  → HUGE number of functionals available
  → bad description of some situations (Van der Waals)
  → empirical character:

$$E_{disp} = -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{C_{ij}}{R_{ij}^6} f_{dmp}(R_{ij})$$
FIG. 3. The alphabet soup of approximate functionals available in a code near you. Figure used with permission from Peter Elliott.

• Ab initio : \( E_a \) at 0 K → Thermochemistry effects:

- Arrhenius/Transition State Theory: \( E_a = \Delta H^\ddagger + 2RT = 4.68 \text{ kcal/mol} \)
• Exp. : more recent work, pseudo second-order reaction:
  \[ \text{HCO} + \text{M} \rightarrow \text{H} + \text{CO} + \text{M}, \text{ pressure not well defined} \]

\[
E_a = \Delta H^\ddagger + RT = 18.59 \text{ kcal/mol}
\]

\[
k_{24} = 10^{11.68(\pm 3.04)} T^{0.66(\pm 1.15)} \times \exp \left[ -7485 \left( \frac{+2360}{-1380} \right) / T \right] \text{ cm}^3/\text{mol/s}
\]

\[
14.87^{+4.69}_{-2.74} \text{ kcal/mol}
\]
Why a barrier?