First-principles thermochemistry for the combustion of TiCl₄ in a methane flame

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5 August 2010
Applications

• Opacifier
• 5 million tonnes per year
Modern applications

- Solar cells
- Kills bacteria under UV light
- Water splitting under UV light
Scanning Electron Microscope

1 µm
Chloride Process

\[ \text{CH}_4(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}_2(g) + \text{O}_2(g) \]

\[ \text{TiCl}_4(g) + \text{O}_2(g) \rightarrow \text{TiO}_2(\text{nanoparticles}) + 2 \text{Cl}_2(g) \]
H$_2$O might be important

- TiO$_2$ can be produced using steam
- H$_2$O highly reactive
- Some industrial evidence that water might influence particle size distribution
- Aim: Investigate stable species that could be formed from reaction with water
Species in literature

- West et al (2009), Combustion and Flame
Species generation

- Take multiplicities from original species
New species

- The algorithm on the previous slide produced over 300 possible species
- A number of these were duplicates
- After duplicates removed we were left with over 200 geometries
- Next step is to screen these species for stable or important molecules
Quantum calculations

\[ \hat{H} \Psi = E \Psi \]

\[ \hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \]
Density Functional Theory

- One to one mapping between ground state electron wavefunction and electron density
- Functional calculates energy given electron density
- Minimise energy to get geometry of ground state
Gaussian

- Gaussian03 used throughout
- We use B97-1/6-311+G(d,p) for geometry optimization and for calculating vibrational frequencies
- 141 species remain
Thermochemistry

• Use data from quantum calculations to calculate thermochemistry (H, S, G etc)
• Rigid rotor harmonic oscillator approximation
• Errors due to enthalpy of formation are the largest
## Enthalpy of formation

- Reasonably sparse literature data
- Choice of reaction critical
- Ideally we could use isodesmic reactions:
  - Number of each bond type unchanged by reaction

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta_f H^\circ_{298.15 \text{K}}$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiOCl</td>
<td>-274</td>
</tr>
<tr>
<td>TiOCl$_2$</td>
<td>-598</td>
</tr>
<tr>
<td>TiOC$_3$</td>
<td>-639</td>
</tr>
<tr>
<td>TiO$_2$Cl$_2$</td>
<td>-558</td>
</tr>
<tr>
<td>TiO$_2$Cl$_3$</td>
<td>-774</td>
</tr>
<tr>
<td>Ti$_2$O$_2$Cl$_3$</td>
<td>-1257</td>
</tr>
<tr>
<td>Ti$_2$O$_2$Cl$_4$</td>
<td>-1552</td>
</tr>
<tr>
<td>Ti$_2$O$_3$Cl$_2$</td>
<td>-1331</td>
</tr>
<tr>
<td>Ti$_2$O$_3$Cl$_3$</td>
<td>-1418</td>
</tr>
<tr>
<td>Ti$_2$O$_2$Cl$_5$</td>
<td>-1272</td>
</tr>
<tr>
<td>Ti$_2$O$_2$Cl$_6$</td>
<td>-1503</td>
</tr>
<tr>
<td>TiCl$_4$</td>
<td>-763.16</td>
</tr>
<tr>
<td>TiCl$_3$</td>
<td>-539.32</td>
</tr>
<tr>
<td>TiCl$_2$</td>
<td>-237.23</td>
</tr>
<tr>
<td>TiCl$_2$</td>
<td>-305.43</td>
</tr>
<tr>
<td>ClOCl</td>
<td>87.86</td>
</tr>
<tr>
<td>OCIO</td>
<td>104.60</td>
</tr>
<tr>
<td>ClOHO</td>
<td>-74.48</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-241.83</td>
</tr>
<tr>
<td>HCl</td>
<td>-92.31</td>
</tr>
<tr>
<td>OH</td>
<td>38.99</td>
</tr>
<tr>
<td>Cl</td>
<td>121.30</td>
</tr>
<tr>
<td>O</td>
<td>249.18</td>
</tr>
</tbody>
</table>

West et. al., Combust Flame, 2009

NIST database
Automatic isodesmic script

• Originally developed for Phadungsukanan et al, J. Phys. Chem. A, 2009, for Si species.
• Express reaction as set of linear equations for each bond.
• Use linear programming package to minimize total bond changes.
Isodesmic reactions

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta_f H_{298.15}^0$_kJ/mol</th>
<th>$\Delta_f H_{298.15}^0$_kJ/mol</th>
<th>Standard Deviation_kJ/mol</th>
<th>No. of reactions</th>
<th>No. of bond changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl$_3$OH</td>
<td>$-941$</td>
<td>$-917$</td>
<td>$14$</td>
<td>$6$</td>
<td>$0$</td>
</tr>
<tr>
<td>Ti$_2$O$_2$Cl$_3$OH</td>
<td>$-1741$</td>
<td>$-1708$</td>
<td>$14$</td>
<td>$4$</td>
<td>$0$</td>
</tr>
<tr>
<td>Ti$_2$OCl$_4$(OH)$_2$</td>
<td>$-1936$</td>
<td>$-1893$</td>
<td>$56$</td>
<td>$6$</td>
<td>$0$</td>
</tr>
<tr>
<td>TiCl$_2$OH</td>
<td>$-719$</td>
<td>$-699$</td>
<td>$24$</td>
<td>$6$</td>
<td>$0$</td>
</tr>
<tr>
<td>TiOClOH</td>
<td>$-742$</td>
<td>$-724$</td>
<td>$34$</td>
<td>$7$</td>
<td>$0$</td>
</tr>
<tr>
<td>TiCl$_2$(OH)$_2$</td>
<td>$-1079$</td>
<td>$-1054$</td>
<td>$28$</td>
<td>$6$</td>
<td>$0$</td>
</tr>
<tr>
<td>TiOCl$_2$OH</td>
<td>$-793$</td>
<td>$-770$</td>
<td>$28$</td>
<td>$6$</td>
<td>$0$</td>
</tr>
<tr>
<td>Ti$_2$O$_3$Cl$_2$OH</td>
<td>$-1545$</td>
<td>$-1518$</td>
<td>$64$</td>
<td>$6$</td>
<td>$0$</td>
</tr>
<tr>
<td>Ti$_2$O$_2$Cl$_2$(OH)$_2$</td>
<td>$-1866$</td>
<td>$-1831$</td>
<td>$43$</td>
<td>$6$</td>
<td>$0$</td>
</tr>
<tr>
<td>TiCl(OH)$_2$</td>
<td>$-850$</td>
<td>$-829$</td>
<td>$29$</td>
<td>$6$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

- Used a script to automatically find isodesmic reactions and take averages
- Main errors due to absence of Ti-H bond in database
Equilibrium compositions

• Cantera
• Use NASA polynomials calculated in this work
• Other polynomials taken from the literature
• NIST/NASA databases
Mole fractions

![Graph showing mole fractions of various compounds as functions of temperature.](image-url)
Collated mole fractions

![Graph showing mole fractions of different species as a function of temperature.]

- $O_xCl_y$ species/HCl
- $TiO_xCl_y$ monomers
- GRI-Mech methane species
- $TiO_xCl_yH_z$ monomers
- $Ti_2O_xCl_yH_z$ dimers
- $Ti_2O_xCl_y$ dimers
Top ten species

- A number of species are present in high concentration
- H likely to influence kinetics
Conclusions

• Hydrogen containing species are stable and will exist at industrial and experimental conditions.

• TiCl$_3$OH, Ti$_2$O$_2$Cl$_3$OH, Ti$_2$OCl$_4$(OH)$_2$, TiCl$_2$OH, TiOCl(OH)$_2$, TiCl$_2$(OH)$_2$, TiOCl$_2$OH, Ti$_2$O$_3$ClOH, Ti$_2$O$_2$Cl$_2$(OH)$_2$, and TiCl(OH)$_2$ are highlighted as ten of the most stable Ti$_i$O$_j$Cl$_k$H$_l$ species for industrial conditions.

• TiCl$_3$OH is the most abundant new species.
Thank you

Welcome to the Computational Modelling Group

Welcome to the website of the CoMo Group. We develop and apply modern numerical methods to problems arising in Chemical Engineering. The overall aim is to shorten the development period from research bench to the industrial production stage by providing insights into the underlying physics and supporting the scale-up of processes to industrial level.

The group currently consists of 25 members from various backgrounds. We are keen to collaborate with people from both within industry and academia, so please get in touch if you think you have common interests.

The group's research divides naturally into two inter-related branches. The first of these is research into mathematical methods, which consists of the development of stochastic particle methods, computational fluid dynamics and quantum chemistry. The other branch consists of research into applications, using the methods we have developed in addition to well-established techniques. The main application areas are reactive flow, combustions, engine modelling, extraction, finite particle synthesis and dynamics. This research is sponsored on various levels by the UK, EU, and industry.

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Poster W4P022