

First-principles thermochemistry for the combustion of TiCl_4 in a methane flame

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and Markus Kraft

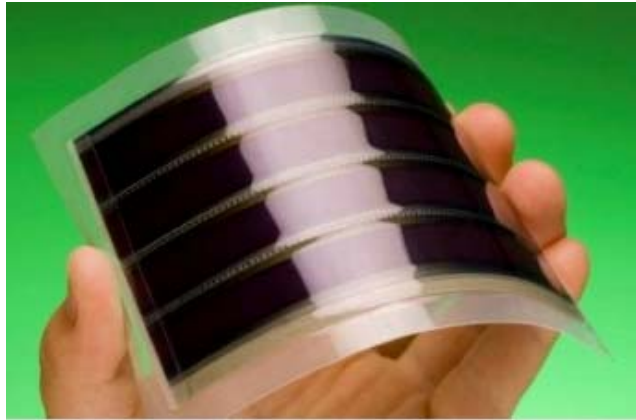
5 August 2010

Applications

- Opacifier
- 5 million tonnes per year



Modern applications



- Solar cells

- Kills bacteria under UV light



- Water splitting under UV light

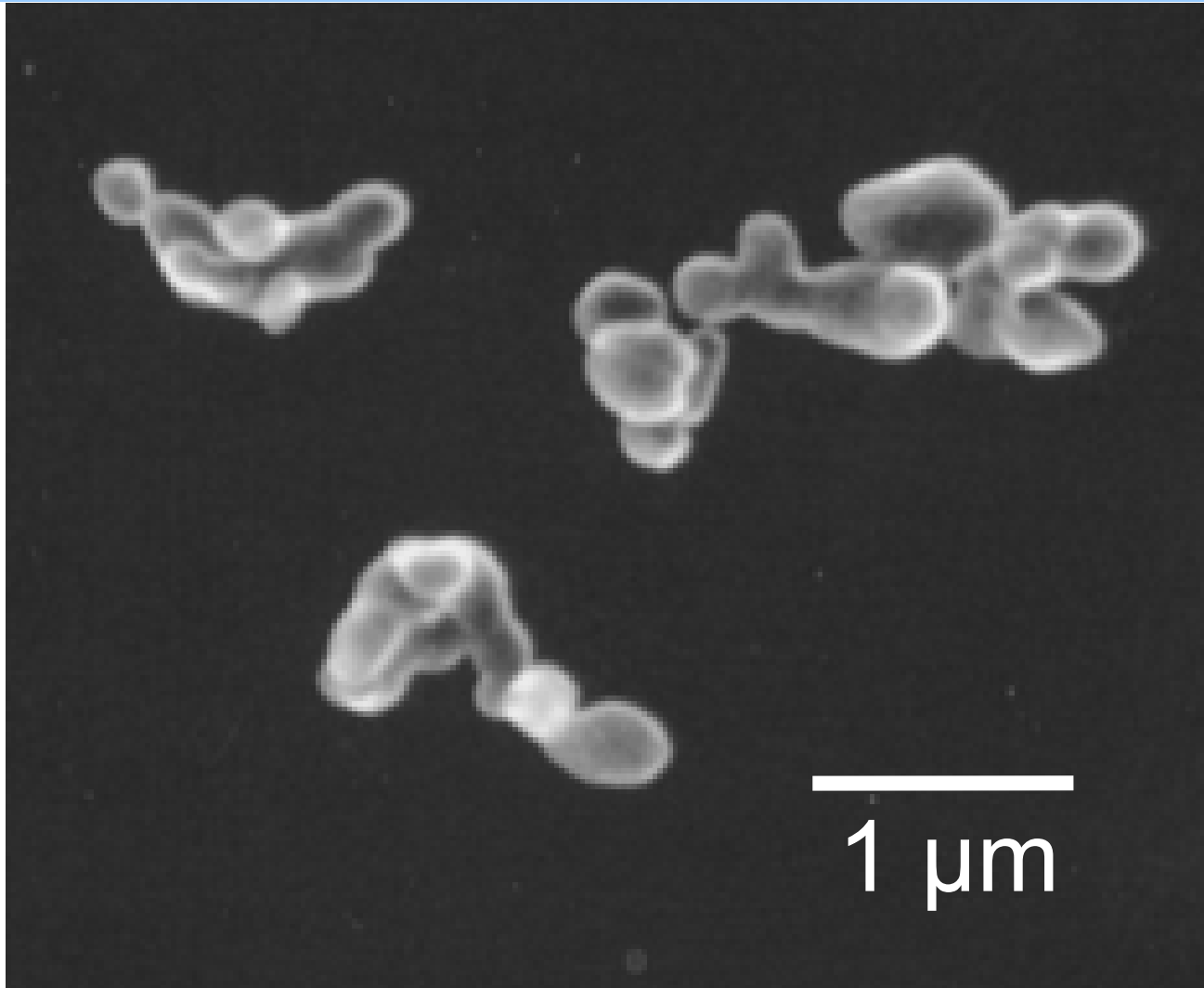


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Scanning Electron Microscope

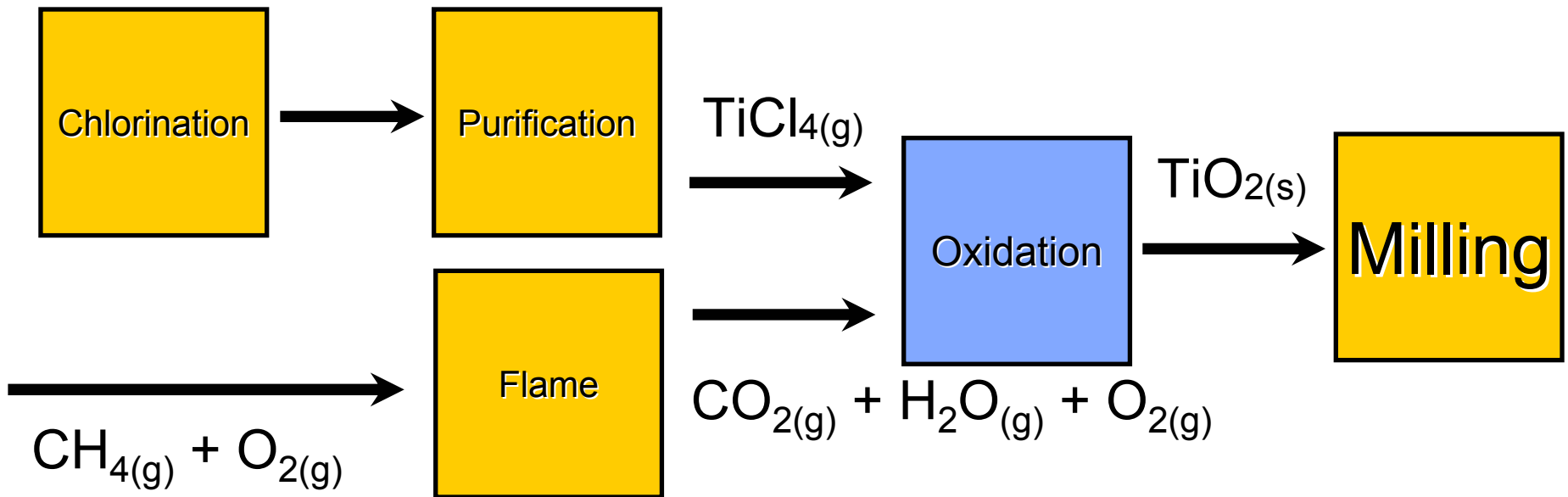


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Chloride Process

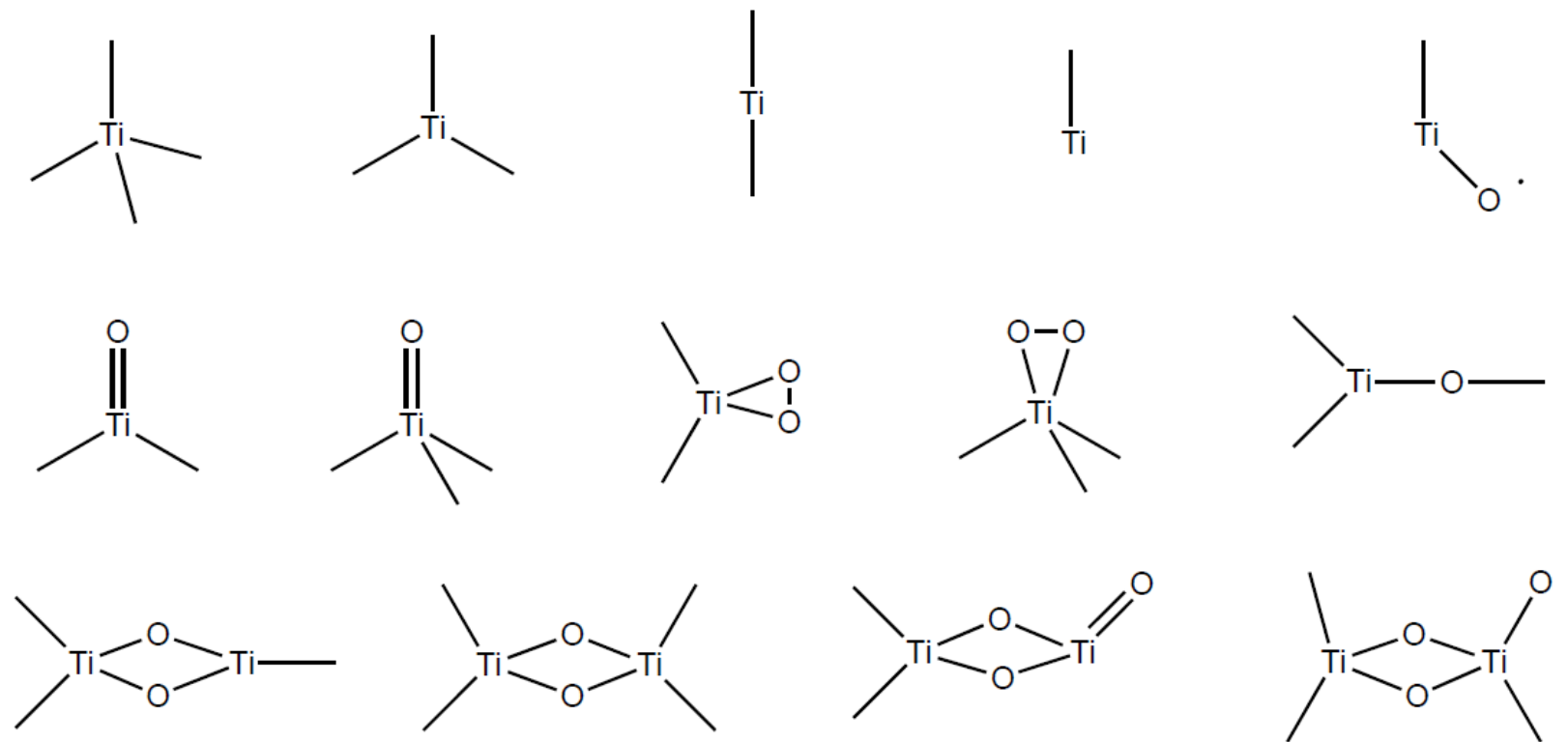


H₂O might be important

- TiO₂ can be produced using steam
- H₂O highly reactive
- Some industrial evidence that water might influence particle size distribution
- Aim: Investigate stable species that could be formed from reaction with water

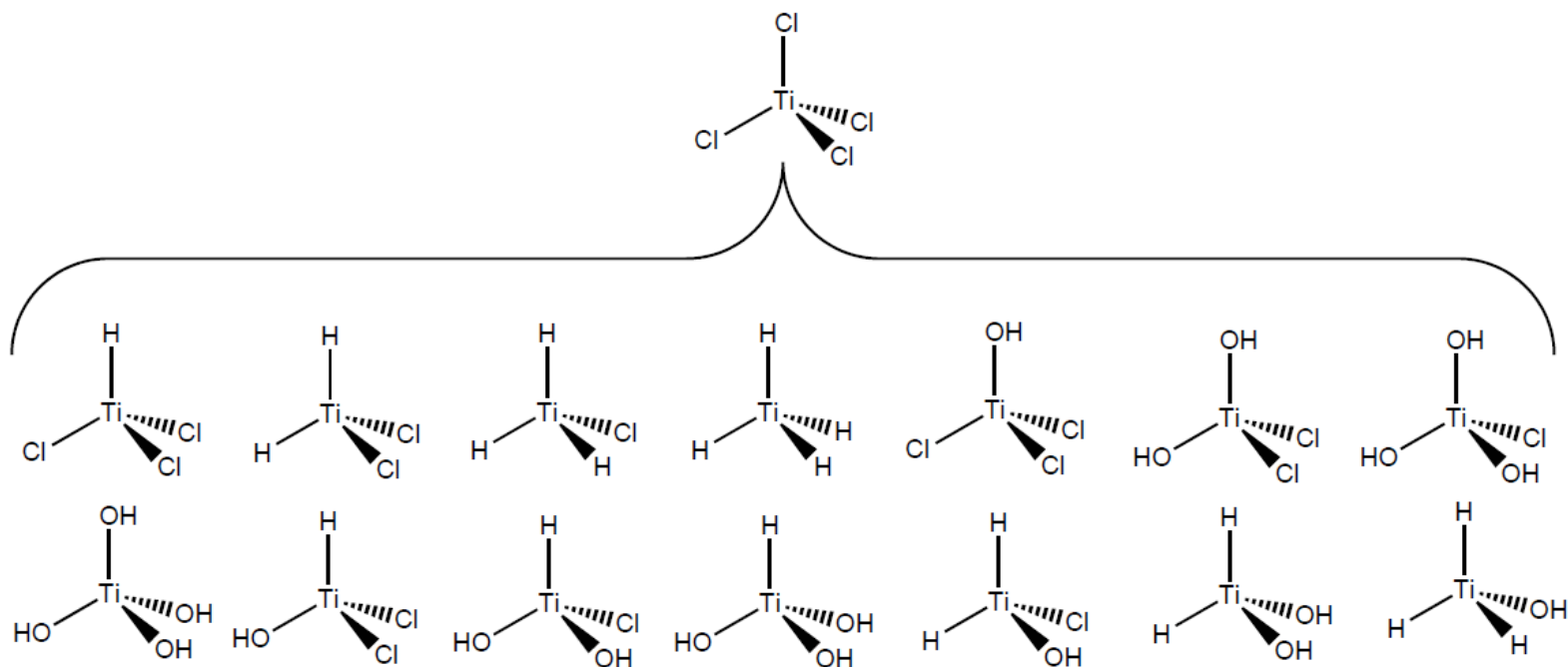


Species in literature



- 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

Species	$\Delta_f H_{298.15\text{ K}}^\circ$ kJ/mol
TiOCl	-274
TiOCl ₂	-598
TiOC ₃	-639
TiO ₂ Cl ₂	-558
TiO ₂ Cl ₃	-774
Ti ₂ O ₂ Cl ₃	-1257
Ti ₂ O ₂ Cl ₄	-1552
Ti ₂ O ₃ Cl ₂	-1331
Ti ₂ O ₃ Cl ₃	-1418
Ti ₂ O ₂ Cl ₅	-1272
Ti ₂ O ₂ Cl ₆	-1503
TiCl ₄	-763.16
TiCl ₃	-539.32
TiCl ₂	-237.23
TiO ₂	-305.43
ClOCl	87.86
OCIO	104.60
ClOH	-74.48
H ₂ O	-241.83
HCl	-92.31
OH	38.99
Cl	121.30
O	249.18

West *et. al.*,
Combust Flame,
2009

NIST database

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



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

Species	$\Delta_f H_{0\text{ K}}^\circ$ kJ/mol	$\Delta_f H_{298.15\text{ K}}^\circ$ kJ/mol	Standard Deviation kJ/mol	No. of reactions	No. of bond changes
TiCl ₃ OH	-941	-917	14	6	0
Ti ₂ O ₂ Cl ₃ OH	-1741	-1708	14	4	0
Ti ₂ OCl ₄ (OH) ₂	-1936	-1893	56	6	0
TiCl ₂ OH	-719	-699	24	6	0
TiOClOH	-742	-724	34	7	0
TiCl ₂ (OH) ₂	-1079	-1054	28	6	0
TiOCl ₂ OH	-793	-770	28	6	0
Ti ₂ O ₃ ClOH	-1545	-1518	64	6	0
Ti ₂ O ₂ Cl ₂ (OH) ₂	-1866	-1831	43	6	0
TiCl(OH) ₂	-850	-829	29	6	0

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

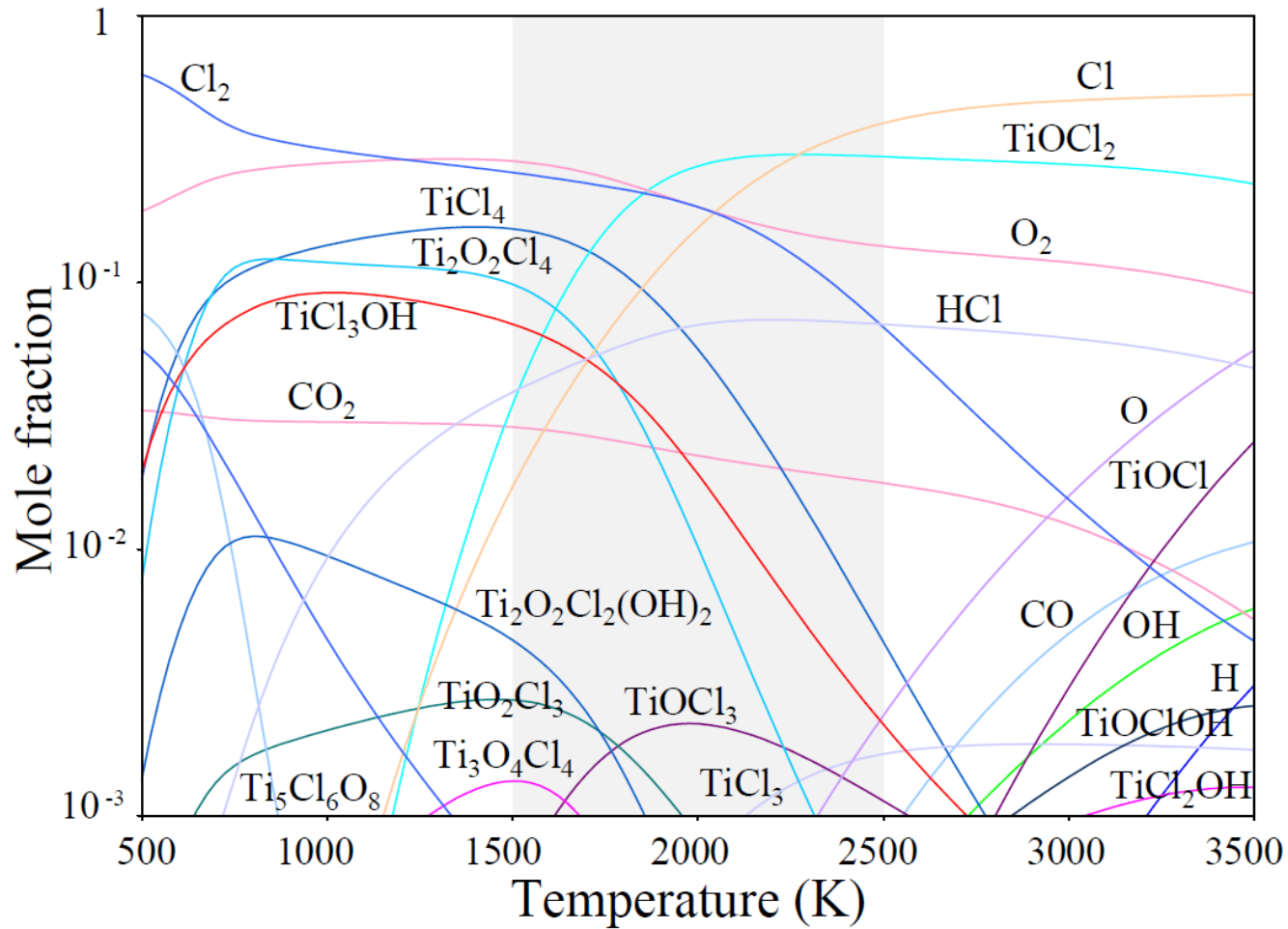


Equilibrium compositions

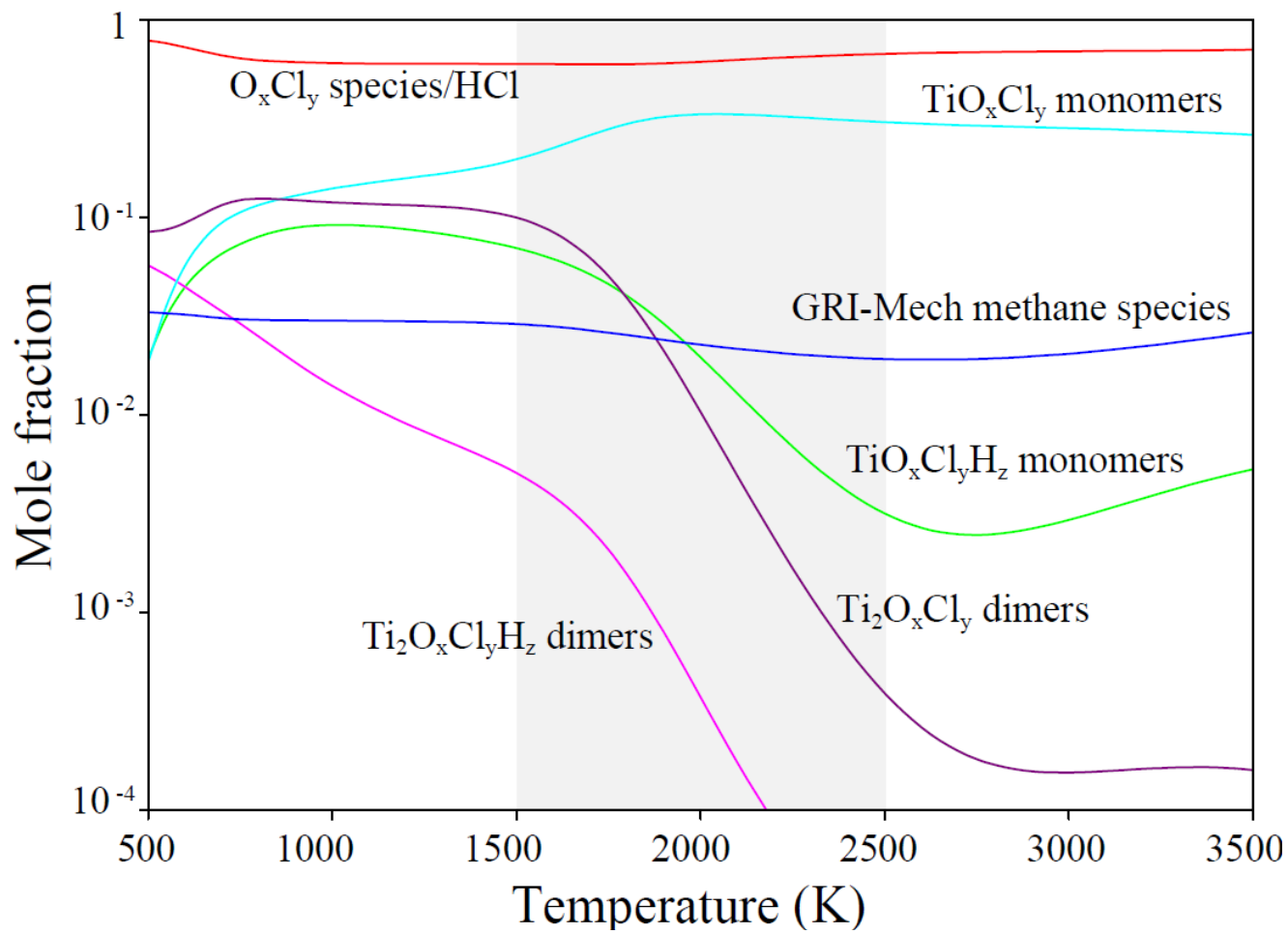
- Cantera
- Use NASA polynomials calculated in this work
- Other polynomials taken from the literature
- NIST/NASA databases



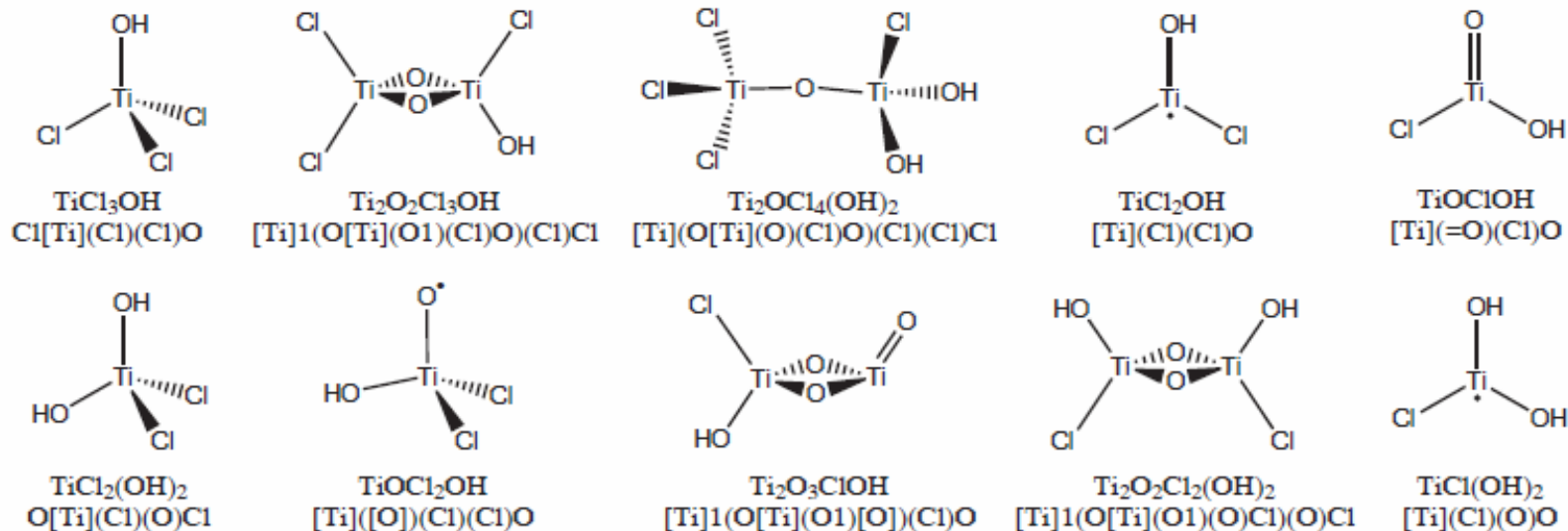
Mole fractions



Collated mole fractions



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_3OH , $\text{Ti}_2\text{O}_2\text{Cl}_3\text{OH}$, $\text{Ti}_2\text{OCl}_4(\text{OH})_2$, TiCl_2OH , TiOClOH , $\text{TiCl}_2(\text{OH})_2$, TiOCl_2OH , $\text{Ti}_2\text{O}_3\text{ClOH}$, $\text{Ti}_2\text{O}_2\text{Cl}_2(\text{OH})_2$, and $\text{TiCl}(\text{OH})_2$ are highlighted as ten of the most stable $\text{Ti}_i\text{O}_j\text{Cl}_k\text{H}_l$ species for industrial conditions.
- TiCl_3OH is the most abundant new species.



Thank you

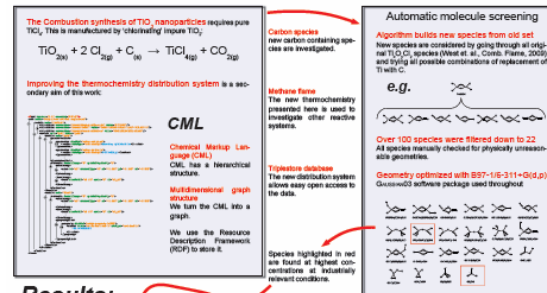


The screenshot shows the CoMo Group website homepage. At the top, there are logos for the University of Cambridge and the CoMo Group. The navigation bar includes links for Home, People, Research, Resources, Preprints, Publications, Conferences, Seminars, and Login. A 'Welcome' message is displayed, followed by a group photo of the CoMo Group members. Below the photo, there is a welcome message and a list of research areas: stochastic particle methods, computational fluid dynamics, and quantum chemistry. The page also features a signature of Markus Kraft, Head of the CoMo Group.

First-principles thermochemistry for gas phase species in an industrial rutile chlorinator

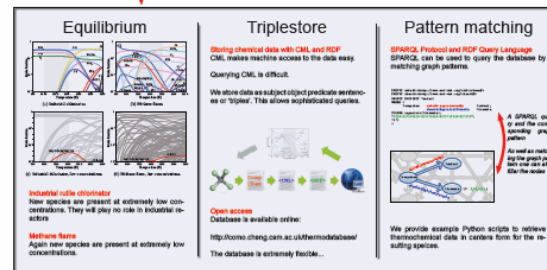
Raphael Shirley, Weerapong Phadungsukanan, Markus Kraft, Jim Downing, Nick Day, and Peter Murray-Rust

<http://como.cheng.cam.ac.uk>



The abstract illustrates the workflow for first-principles thermochemistry. It starts with the combustion synthesis of TiO₂ nanoparticles, represented by the reaction: $TiO_{2(s)} + 2 Cl_{2(g)} + C_{(s)} \rightarrow TiCl_{4(g)} + CO_{2(g)}$. This is followed by improving the thermochemistry distribution system. The workflow involves using the Chemical Markup Language (CML) to represent the chemical structure, which is then converted into a graph. The graph is used to perform automatic molecule screening, where new carbon-containing species are investigated. The screening process involves building new species from an old set, checking for physico-chemically unreasonable geometries, and optimizing the geometry with the B3LYP-6-311++(d,p) Gaussian03 software package. The results show that over 100 species were filtered down to 22, with 10 species highlighted in red as being found at highest concentrations at industrially relevant conditions.

Results:



The Results section is divided into three main areas: Equilibrium, Tripestore, and Pattern matching. Equilibrium shows plots of species concentration versus time for various species. Tripestore discusses the integration of chemical data with CML and RDF, highlighting the challenges of querying CML and the benefits of RDF. Pattern matching shows the use of SPARC, a protocol and RDF query language, to retrieve thermochemical data in a format suitable for matching graph patterns. The results also mention that the database is extremely facile and that the group provides example Python scripts to retrieve thermochemical data in various forms for the resulting species.

1. There is very little chemical interaction between Ti and Cl in industrial rutile chlorinators.
2. These new species also play no role in the flame synthesis of TiO₂. Water is the only important reactant.
3. Using an RDF database for the dissemination of thermochemical data offers significant advantages.

Many thanks to St Edmund's College, Cambridge and The Cambridge Commonwealth Trust.

<http://como.cheng.cam.ac.uk>

Poster W4P022