Engler-Bunte-Institut Teilinstitut Verbrennungstechnik (EBI-vbt)

Chemischer Gleichgewichtsrechner

Probieren Sie auf dieser Seite unser Programm für die Berechnung des thermodynamischen Gleichgewichtes einer Gasmischung mehr ...

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MCS 10 - Vortrag

Bockhorn, H.: "Some notes on challenges of combustion in future energy systems". mehr ...

Bachelor- und Masterarbeiten

Aktuelle Angebote für das Anfertigen von Bachelor- und Masterarbeiten finden sie auf der folgenden Seite. mehr ...

Development of Reaction Mechanism by Quantum Chemistry methods
Application of computational quantum chemistry (ab initio and DFT calculations) is used to estimation of thermochemical properties and kinetic parameters of small and large species, including biochemicals, large aromatic intermediates in soot formation, carbon nanotubes and many other systems.

**Introduction**

Aromatic and poly-aromatic compounds are important components of fuels. They are also formed in pyrolysis reactions and in fuel rich regions of flames and other thermal systems, where they are considered important precursors and intermediates in soot and PAH formation. The decomposition products of these species in combustion and oxidation reactions involve the incorporation of oxygen through reactions with oxygenated radicals and with molecular oxygen forming species like hydroperoxides or unsaturated oxy-hydrocarbon.

This work involves the development of an extensive thermochemical property data base on unsaturated (olefinic, acetylenic and aromatic) oxygenated hydrocarbon chemical species: enthalpy of formation, bond energies, standard entropy and heat capacity data as a function of temperature are calculated. These data serves the modelling communities in the area of atmospheric chemistry, combustion, industrial processes relating to synthesis and use in synthesis of hydroperoxides, peroxy and peroxy radical species. These parameters are available over a wide range of temperature (200 to over 5000 K) which can be applied to all of the above areas.

Peroxides and peroxy species are perhaps the most important intermediates in all low and moderate (1200 Æ 1300 K) combustion and in atmospheric photochemical oxidation processes of hydrocarbons and derivatives. Examples of the importance of these peroxy and peroxy intermediates include: control of self ignition in internal combustion engines (knock in spark ignited engines plus fuel ignition in diesels and in the new and upcoming HCCI engines. The peroxy radical reaction chemistry also controls the negative temperature behavior of hydrocarbons where there is a competition between the complex chain branching paths and termination reactions. Alkyl hydroperoxide species are also important in limiting soot formation and in soot burn-out in hydrocarbon pyrolysis and combustion.

A very significant quantity of thermochemical parameters are generated for stable molecules, intermediate radicals and transition state structures of oxygenated hydrocarbon molecules, particularly unsaturated and aromatic carbon Æ oxygen systems.

**Example of Work**

One example of oxidative destructive in aromatics involves conversion of dibenzofurans and / or dioxins in combustion systems. The destruction of the aromatic moiety often starts with loss of a phenyl hydrogen, through abstraction by radical pool species, such as H, O, OH, or Cl, forming a phenyl or benzofuranyl radical. This occurs even at moderate temperatures in downstream zones of an incinerator. The phenyl radicals will rapidly react with molecular oxygen in the combustion environment to form an energized (phenyl peroxy) adduct, which can undergo further reaction through several pathways. Figure 1 illustrates some of the intermediate products from decomposition reactions (beta scission (unzipping) and oxidation) of a benzofuran di-aldehyde formal radical, which is estimated is the major product from reaction of molecular oxygen with a dibenzofuran Æ phenyl radical. The decomposition reaction results in a number of intermediates and radical products, which do not have thermochemistry or groups for use in group additivity estimations. Knowledge of the thermochemical properties of these species is important to understanding the decomposition and oxidation pathways of these intermediates, which result from initial oxidative ring opening of the aromatics.
For such larger molecules, high level, calculation techniques are computationally expensive or not possible. Density Functional Theory may be one of the few applicable calculation methods for these large molecules systems.
Computational Method

All of the calculations are performed using the Gaussian 03 program suite, which calculates the total energies, the frequencies and moment of inertia. The determination of the entropies and heat capacities are calculated with the help of two codes: SMCPS and ROTATOR.
Publications

―Experimental and Numerical Investigation of the Degradation of Chlorinated Hydrocarbons in Incineration Systems―

Thermodynamic Properties ($S(298)$, $Cp(T)$), Internal Rotations and Group Additivity Parameters in Vinyl and Phenyl Hydroperoxides

Structures, Thermochemical Properties (Enthalpy, Entropy and Heat Capacity), Rotation Barriers, Bond Energies of Vinyl, Allyl, Ethynyl and Phenyl hydroperoxides

Thermochemical Properties, Rotation Barriers, and Group Additivity for Unsaturated Oxygenated Hydrocarbons and Radicals Resulting from Reaction of Vinyl and Phenyl Radical Systems with $O_2$

Enthalpy of Formation and Bond Energies on Unsaturated Oxygenated Hydrocarbons using G3MP2B3 Calculation Methods

Thermodynamic and Ab Initio Analysis of the Controversial Enthalpy of Formation of Formaldehyde

Thermodynamic Properties of the Species Resulting from the Phenyl Radical with $O_2$ Reaction System

Thermochemical similarities among three reaction systems:
Vinyl $O_2$ Æ Phenyl $O_2$ Æ Dibenzofuranyl $O_2$
šReaction of Phenyl Radical with \( O_2 \): Thermodynamic Properties, Important Reaction Paths and Kineticsš

šReaction of Dibenzofuran radical with \( O_2 \)š

šThe Phenyl \( O_2 \) Reaction: Thermodynamics and kineticsš

šThermochemical similarities among three reaction systems: Vinyl \( O_2 \) Æ Phenyl \( O_2 \) Æ Dibenzofuranyl \( O_2 \)š
Sebbar, N.; Bozelli, J. W.; Bockhorn, H.

šThe oxidation reaction of \( C_6H_5C\cdot(=O) \) radicalš
Sebbar, N.; Bozelli, J. W.; Bockhorn, H.
Sixth Mediterranean Combustion Symposium Æ MCS6, Ajaccio ,Corsica, France, June 7-11, 2009

Presentations

šReaction of Phenyl Radical with \( O_2 \): Thermodynamic Properties, Important Reaction Paths and Kineticsš
Joseph Bozelli, Nadia Sebbar, William Pitz and Henning Bockhorn
The 2\(^{nd}\) Joint Meeting of the US Sections of the Combustions Institute, Oakland, California, March 25-28, 2001

šReaction of Phenyl Radical and Dibenzofuran with \( O_2 \): Thermodynamic Properties, Reaction Pathways, Kinetics and Initial Steps for Dibenzofuran Oxidationš
Nadia Sebbar, Henning Bockhorn and Joseph W. Bozelli
"Reaction of Phenyl Radical and Dibenzofuran with O\textsubscript{2}"

Nadia Sebbar, Henning Bockhorn and Joseph W. Bozzelli

Joint Meeting of the Belgian and Dutch Sections of the Combustion Institute, Brussels Belgium. April 2002.

"Thermochemical and Kinetic Analysis: Oxidation of Aromatics - Benzene, Toluene, Xylene"

Bozzelli, J. W.; da Silva, G.; Chen, C-C.; Sun, H.; Sebbar, N.; Bockhorn, H.


"Numerical Investigation of the Dibenzofuranyl O\textsubscript{2} Reaction System: Thermodynamics, Kinetics, and Reaction Paths"

Sebbar, N.; Bockhorn, H.; Bozzelli, J. W.


"An Elementary Mechanism for the Oxidative Degradation of Dibenzofuran"

Nadia Sebbar and Henning Bockhorn,


"Thermochemical Similarities among Three Reaction Systems: Vinyl O\textsubscript{2} Ç Phenyl O\textsubscript{2} Ç Dibenzofuranyl O\textsubscript{2}"

Nadia Sebbar, Henning Bockhorn and Bozzelli, J. W.


"The Oxidation of Dibenzofuranyl: Thermodynamic Properties and Reaction Pathways"

Nadia Sebbar, Henning Bockhorn and Bozzelli, J. W.,

20\textsuperscript{th} International Conference on Chemical Thermodynamics August 3-8, 2008, Warsaw, Poland.

Posters
Products

Petra Bonni, Leonhard Rutz, Nadia Sebbar and Henning Bockhorn


Atomized Validation of a Detailed Mechanism for the Description of Dioxins Formation and other by products
Nadia Sebbar, Jörg Appel and Henning Bockhorn

The Combustion Institute, Joint Meeting of the British, German and French Sections. 18–21 May, Nancy, France, 1999

Atomized Validation of a Detailed Mechanism for the Description of Dioxins Formation and other by products
Nadia Sebbar, Jörg Appel and Henning Bockhorn

The Sixth International Congress on Toxic Combustion By-products. June 27–30, 1999, University of Karlsruhe, Germany.

Reaction of Phenyl and Dibenzofuran Radicals with O₂: Thermodynamic Properties, Reaction Pathways and kinetics
Nadia Sebbar, Henning Bockhorn and Joseph, W. Bozzelli.

The combustion Institute, 28th International Symposium on Combustion, 30 July–4 August, 2000, Edinburgh, Scotland

Thermodynamic properties (Enthalpies, Entropies and Heat Capacities) and Reactions of Vinyl Hydroperoxides, peroxy radicals and phenyl hydroperoxides
Nadia Sebbar, Henning Bockhorn and Joseph, W. Bozzelli.

Seventh International Congress on Toxic Combustion By-Products. June 4–6, 2001, Research Triangle Park, North Carolina USA

Thermodynamic properties (Enthalpies, Entropies and Heat Capacities) and Reactions of Vinyl hydroperoxides, peroxy radicals and phenyl hydroperoxides
Nadia Sebbar, Henning Bockhorn and Joseph, W. Bozzelli.

5th International Conference on Chemical Kinetics, 16–20 July 2001, National Institute of standards and Technologies, Gaithersburg, MD USA

Thermodynamic properties and reactions of vinyl hydroperoxides and phenyl hydroperoxides
Nadia Sebbar, Henning Bockhorn and Joseph, W. Bozzelli.
Formation and Degradation of Hydrocarbons in High-Temperature Reactions, October 2001

Über die Reaktion von Phenylradikal mit O$_2$: Thermodynamische Eigenschaften, Reaktionswege, Kinetik und Anfangsschritte für Dibenzofuran.


Deutsche Bunsen-Gesellschaft für Physikalische Chemie. 77th International Discussion Meeting


Über die Reaktion von Phenylradikal mit O$_2$: Thermodynamische Eigenschaften, Reaktionswege und Kinetik.

Nadia Sebbar und Henning Bockhorn, Chiung-ju Chen und Joseph, W. Bozzelli.

17th International Symposium on Gas Kinetics, Essen, August 24-29, 2002.

Über die Reaktion von Dibenzofuranradikal mit O$_2$: Thermodynamische Eigenschaften, Reaktionswege und Kinetik.


Über die Entwicklung einer umfassenden Thermochemischen Datenbank auf ungesättigte oxyzentierte Kohlenwasserstoffartefakte.


The 10th International Congress on Combustion by-Products: Origin, Fate and Health Impacts, Ischia, Italy, June 17-20, 2007.