Photoelectron Photoion Coincidence Spectroscopy to Unveil Reaction Mechanisms by Isomer-selective Detection of Elusive Molecules: From Combustion to Catalysis

Patrick Hemberger* and Andras Bodi

*SCS-DSM Award for best poster presentation in Catalysis Science & Engineering

Abstract: Elusive and reactive intermediates, such as radicals, play a central role in reaction mechanisms. Photoelectron photoion coincidence spectroscopy with tunable vacuum ultraviolet synchrotron radiation offers a multiplexed, sensitive, mass- and isomer-selective way to identify and, in some cases, determine mole fractions of reactive species. It thus helps to unveil the missing link(s) between reactants and products. After a brief overview of the technique, we review two systems in three different reactive environments. First, the unimolecular decomposition mechanism of ortho-xylyl radicals is revealed in pyrolysis experiments. Second, the insights gained are used to analyze a fuel-rich meta-xylene flame, which suggests that important xylyl isomerization reactions are currently missing in combustion models. Third, photoion mass-selected threshold photoelectron spectra identify the fulvenone ketene as the crucial intermediate in the catalytic fast pyrolysis of a lignin model compound and help map heterogeneous catalysis mechanisms.

Keywords: Photoelectron spectroscopy · Pyrolysis · Reaction mechanism · Reactive intermediates · Vacuum ultraviolet synchrotron radiation

Patrick Hemberger obtained his PhD in physical chemistry from University of Würzburg, Germany on the photoionization of radicals and carbenes with synchrotron radiation and optical lasers. He joined Paul Scherrer Institute as a beamline scientist in 2011 and is currently also principal investigator in a Swiss Federal Office of Energy (BFE) project about combustion chemistry. His research interests are reaction dynamics and mechanisms in high-energetic environments such as combustion and catalysis. To unveil these insights, he probes reactive molecules isomer-selectively using vacuum ultraviolet synchrotron radiation, ultrafast lasers, combined with photoelectron spectroscopy and mass spectrometric techniques.

Introduction

Combustion is here to stay: even after discounting automotive uses, it is responsible for almost 50% of the energy consumption in Switzerland.[1] Thus, we have to address its downsides, such as greenhouse gas, NOx and soot emissions. Apart from the engineering approach to pursue advanced motor and exhaust concepts, such as homogeneous charge compression ignition (HCCI), or selective catalytic reduction (SCR), harmful emissions may be also mitigated with the help of a fundamental understanding of combustion chemistry and kinetics. Such knowledge also helps to settle abatement strategies and introduce emission standards.[2] Combustion is initiated by free radical reactions, and ignition is particularly sensitive to the radical concentrations. A detailed knowledge of the radical concentrations is therefore imperative to develop predictive combustion models for established and alternative fuels. Standard chemical analysis techniques, e.g. gas chromatography combined with mass spectrometry (GC/MS), only detect stable species, due to long sample residence times and rapid quenching of elusive species.

Molecular beam[3] mass spectrometry (MS) coupled with vacuum ultraviolet (VUV) synchrotron radiation has emerged as a versatile tool to trace transient species formed in gas-phase reactions in flames,[5] reactors[6] and heterogeneously catalyzed processes directly.[4b,7] Thanks to the rapid expansion into high vacuum, high dilution in an inert buffer gas and adiabatic cooling, quenching processes can be greatly suppressed.[3] Dissociative ionization can be controlled by tuning the photon energy between 5–30 eV, or 250–41 nm when recording photoionization mass spectra (PIMS). The energy dependence of PIMS allows us to distinguish, e.g. methyl ions formed by direct ionization of methyl radicals from those formed by fragmentation of ionized methane. Fig. 1 shows PI spectra of meta- and para-xylyl (methylbenzyl) radicals in blue. Although the different ionization onsets, 6.9 vs. 7.0 eV, suf-
fic to identify pure samples when combined with state-of-the-art calculations, the lack of spectral features make it difficult to characterize mixtures or identify constitutional isomers if the ionization energies are close by. Since combustion environments often contain a plethora of species, this limits the selectivity of PIMS.

### Photoion Photoelectron Coincidence Spectroscopy

Imaging photoelectron photoion coincidence spectroscopy (iPEPICO) can be used to recover the necessary spectral selectivity to address this issue by virtue of photoelectron spectroscopy. Photoelectrons are velocity map imaged and detected according to their velocity on a fast position sensitive detector. The most easily tunable VUV sources, synchrotrons, deliver quasi-continuous light and the promptly detected electron also acts as start signal for the time-of-flight mass analysis of the coincident photoion. By correlating threshold (near-zero kinetic energy) photoelectrons with ions from the same ionization event, photoion mass-selected threshold photoelectron spectra (ms-TPES) are obtained. This additional analytical dimension is highly beneficial because vibrational transitions follow the Franck–Condon (FC) principle, i.e. are governed by the nuclear wave function overlap of the initial neutral and final ion state. Thus, ms-TEPES spectra constitute an isomer-specific spectroscopic fingerprint and can easily be simulated.

In Fig. 1, TPE spectra of meta- and para-xylal radicals are presented in black along with FC simulated photoelectron spectra. The activity of a ring deformation mode upon ionization is nicely reproduced by the FC simulation and used together with the adiabatic ionization energy (arrows) for the assignment of each individual isomer.

PEPICO was originally developed by Brehm and von Puttkammer to investigate the unimolecular dissociation of ions.[8] It has been improved continuously as a spectroscopic tool and to map the phase space and the flow of reactive flux in internal energy selected ions.[9] Imaging PEPICO experiments are found at third-generation synchrotron facilities,[10] where they are used to investigate chiral systems,[10a] to derive highly accurate thermochemistry,[11] to understand impulsive and statistical fragmentation processes and map complex fragmentation pathways.[12] Despite low number densities and difficult preparation, PEPICO has been used to record photoelectron spectra of numerous short-lived radical species at high intensity light sources, including the VUV beamline at the Swiss Light Source, for more than a decade.[13] These spectra serve to detect elusive species directly in high-energy environments like flames and reactors or to gain insight into their thermochemistry.[14]

For instance, accurate heats of formation were obtained for reactive m-xylene diradicals (7 in Scheme 1) as well as for photolytically produced methyl peroxo species.[15,16]

Furthermore, the high energy resolution, dynamic range, and fragment-free ionization make PEPICO a universal, sensitive and selective analytical tool for the isomer-selective detection of elusive gas-phase intermediates in complex reactive environments.[10c,17,18] Here, we would like to present two recent topics in detail.

First, xylene flame chemistry was studied by following the fate of xylal radicals upon unimolecular decomposition and in a fuel-rich xylene flame. Second, thanks to detecting the fulvene intermediate, we could establish the catalytic fast pyrolysis mechanism of guaiacol, a lignin model compound.

### Pyrolysis and Combustion

Aromatic compounds represent more than 45 vol% in conventional fuels, and are responsible for the high octane ratings in modern gasoline. Due to health issues, benzene is regulated in fuels in Europe and the US[19] and is replaced by toluene and xylenes. It is widely accepted that xylenes form xylal radicals (C₆H₃) upon fuel decomposition in internal combustion engines. However, questions arose about the potentially divergent reactivity of the three xylal isomers.[20] Kinetic experiments in shock tubes[21] supported the conclusion that ortho- (2, Scheme 1) and para-xylal (4) decompose by hydrogen atom loss at a much faster rate than meta-xylal (3). Evidently, elementary reactions, such as fuel destruction pathways, need to be fully understood to develop predictive combustion models. Pyrolysis reactors (see Scheme 1) are ideally suited to investigate the thermal decomposition of reactive molecules,[22] Xylylbromides (C₆H₃Br, 1a,b,c see Scheme 1) produce xylal radicals 2, 3, 4 isomer-selectively upon thermal decomposition.[23] The gas sample leaves the hot micro reactor (Scheme 1) to form a molecular beam, which is ionized by incident VUV radiation and both ions and electrons are detected.

Threshold photoelectron spectra in Fig. 1 confirm the isomer-selective generation of m- and p-xylal radicals at m/z = 105, based on their different vibrational fingerprints. With the help of their distinctly different ms-TPES, the fate of the fuel radicals can be followed isomer-selectively as a function of the reaction temperature. As the temperature increases in the reactor, hydrogen atom loss is observed to yield m/z = 104 (shown for o-xylal in Fig. 2a) and the corresponding ms-TEPES spectra provide the necessary isomer information (see Fig. 2b). At low reactor temperatures, o-xylalene (5) and benzocyclobutene (8) are observed at m/z = 104. The reaction mixture changes fundamentally above 1000 K (upper trace in Fig. 2b): o-xylalene (5) is depleted, and p-xylalene (6) and styrene (9) are identified as additional components (Scheme 1). While formation of o-xylalene (5) and benzocyclobutene (8) is explained by hydrogen loss and a subsequent ring closure reaction,[23,24] styrene

![Fig. 1. Photoionization spectra (in blue) and threshold photoelectron spectra (in black) of meta- and para-xylal radicals. In contrast with the slowly rising PIMS, offset by the difference in ionization energy, isomer-specific vibrational transitions are clearly evident in the TPES and can be modeled by calculating Franck–Condon factors (in red).](image-url)
Thanks to the low pressure, the flame zone height above burner is stretched and a quartz glass sampling cone is used to continuously sample from the flame (see Fig. 3b). A molecular beam is formed here, which preserves the threshold ionization matrix, in which the threshold electron signal is plotted as a function of photon energy and coincident photoion m/z ratio. The ms-TPE spectrum and FC simulation of m/z = 104 (Fig. 3, center) reveals p-xylylene (6), benzocyclobutene (8) and styrene (9) in the flame environment, while the m-xylylene diradical (7) was generally absent. Nonetheless, a neat m-xylyl pyrolysis experiment, analogous to the one shown in Fig. 2 for o-xylyl, revealed the same composition of reactive C6H6 isomers, which implies that the same chemistry drives these processes both in pyrolysis and in the flame.\cite{[28]} While ortho-4 and para-xylyl (2) putatively lose hydrogen by simple C-H bond cleavage, the same reaction would lead to a diradical 7 in the case of the meta isomer 3.\cite{[28]} Da Silva \textit{et al.} suggested, based on calculations, that m-xylyl (3) first rearranges to the ortho-2 or para-isomer 4 prior to hydrogen atom loss.\cite{[23]} Thereafter, stable species, e.g. p-xylylene (6), benzocyclobutene (8) and styrene (9) are yielded.\cite{[23,24b,28]} This may also explain the reduced reactivity and the slower burning velocity of m-xyylene.

Height above burner scans can be employed to determine the concentration profiles of reactive intermediates directly (see Fig. 3b,c).\cite{[30]} Fig. 3c compares the experimental mole fraction of m-xylyl as a function of the height above burner with five different combustion models shown in dashed lines.\cite{[31]} Interestingly, the concentration of the fuel radical is overestimated by all kinetic models, which may indicate that the isomerization channel, also found upon pyrolysis of the radicals, plays an important role in flames.\cite{[29]}

Xylyl radicals are relatively inactive towards oxidation due to their aromatic character, and can generate polycyclic aromatic

\begin{align*}
\text{(9) and p-xylylene (6) generation can be rationalized by calculating the C6H6 potential energy surface which connects 9 and 5 over a carbene intermediate.}^\text{[23]}\text{ Production of 6 can be explained by an equilibration of the xylyl radical at very high temperatures and subsequent hydrogen atom loss (Scheme 1). However, note the absence of the H-loss product from m-xylyl, to be discussed later. Although these processes are purely unimolecular, the underlying chemistry is already quite complex and photoelectron photoion coincidence spectroscopy, supported by \textit{ab initio} calculations, could identify the reaction mechanism leading to combustion-relevant radical intermediates and products.}
\end{align*}

Combustion processes represent a complex interplay between a plethora of chemical reactions and fluid dynamics. Therefore, the importance of unimolecular reactions, such as the xylyl mechanism, may be questioned as far as the decomposition of radical intermediates in actual flames is concerned. In a collaboration with the University of Duisburg/Essen and the German Aerospace Center, we coupled a McKenna-type burner, operated at ca. 40 mbar, to the PEPICO apparatus to study flames directly (see Fig. 3b).\cite{[25]} Thanks to the low pressure, the flame zone is stretched and a quartz glass sampling cone is used to continuously sample from the flame (see Fig. 3b).\cite{[16,26]} A molecular beam is formed here, too, which preserves reactive intermediates.

Different flame zones are sampled in height above burner scans by moving the sampling cone with respect to the burner surface, probing the reactant fuel and oxygen near the burner, the reactive intermediates in the reaction zone, or the exhaust (CO, CO\textsubscript{2}, H\textsubscript{2}O, see Fig. 3b) farthest away. Among xylenes, the flame of the meta-isomer exhibits the slowest burning velocity,\cite{[27]} which motivated us to investigate its fuel destruction and soot formation pathways. The m-xylyl radical was found to be the most abundant C6H6 radical species in a m-xyylene/oxygen/argon flame at a stoichiometry of 1.79. However, a minor amount of p-xylyl radicals may also be present in the reaction mixture.\cite{[28]} It is interesting to compare the hydrogen loss dynamics from m-xylyl radicals in the flame with our findings in the pyrolysis reactor. Fig. 3a shows the threshold energy surface which connects 9 and 5 over a carbene intermediate.\cite{[23]} Production of 6 can be explained by an equilibration of the xylyl radical at very high temperatures and subsequent hydrogen atom loss (Scheme 1). However, note the absence of the H-loss product from m-xylyl, to be discussed later. Although these processes are purely unimolecular, the underlying chemistry is already quite complex and photoelectron photoion coincidence spectroscopy, supported by \textit{ab initio} calculations, could identify the reaction mechanism leading to combustion-relevant radical intermediates and products.

\begin{align*}
\text{Combustion processes represent a complex interplay between a plethora of chemical reactions and fluid dynamics. Therefore, the importance of unimolecular reactions, such as the xylyl mechanism, may be questioned as far as the decomposition of radical intermediates in actual flames is concerned. In a collaboration with the University of Duisburg/Essen and the German Aerospace Center, we coupled a McKenna-type burner, operated at ca. 40 mbar, to the PEPICO apparatus to study flames directly (see Fig. 3b).}^\text{[25]}\text{ Thanks to the low pressure, the flame zone is stretched and a quartz glass sampling cone is used to continuously sample from the flame (see Fig. 3b).}^\text{[16,26]}\text{ A molecular beam is formed here, too, which preserves reactive intermediates.}
\end{align*}

\begin{align*}
\text{Different flame zones are sampled in height above burner scans by moving the sampling cone with respect to the burner surface, probing the reactant fuel and oxygen near the burner, the reactive intermediates in the reaction zone, or the exhaust (CO, CO\textsubscript{2}, H\textsubscript{2}O, see Fig. 3b) farthest away. Among xylenes, the flame of the meta-isomer exhibits the slowest burning velocity,}^\text{[27]}\text{ which motivated us to investigate its fuel destruction and soot formation pathways. The m-xylyl radical was found to be the most abundant C6H6 radical species in a m-xyylene/oxygen/argon flame at a stoichiometry of 1.79. However, a minor amount of p-xylyl radicals may also be present in the reaction mixture.}^\text{[28]}\text{ It is interesting to compare the hydrogen loss dynamics from m-xylyl radicals in the flame with our findings in the pyrolysis reactor. Fig. 3a shows the threshold energy surface which connects 9 and 5 over a carbene intermediate.}^\text{[23]}\text{ Production of 6 can be explained by an equilibration of the xylyl radical at very high temperatures and subsequent hydrogen atom loss (Scheme 1). However, note the absence of the H-loss product from m-xylyl, to be discussed later. Although these processes are purely unimolecular, the underlying chemistry is already quite complex and photoelectron photoion coincidence spectroscopy, supported by \textit{ab initio} calculations, could identify the reaction mechanism leading to combustion-relevant radical intermediates and products.}
\end{align*}
Fig. 3. a) Threshold photoionization matrix recorded in a meta-xylene/oxygen/argon flame at a stoichiometry of 1.79. Bright spots correspond to strong FC allowed transitions of specific isomers. Photon mass-scaled TPE spectra can be obtained by integrating a specific mass-to-charge ratio. Methyl-cyclopentadienes (m/z = 80), p-xylene, styrene, benzocyclobutene (m/z = 104), indene, m-methyl-phenylacetylene and 3-phenylpropyne (m/z = 116) can be identified by their respective ms-TPE spectra (white open circles) and calculated FC factors (red lines). b) Picture of the flame and sampling cone. By varying the distance of the sampling cone to the burner surface different flame regions (reactants, intermediates and products) can be probed. c) Flame profile of meta-xyyl together with five different kinetic models, which overestimate the concentration of the radical species.

hydrocarbons (PAHs), the precursors of soot. Upon combustion of m-xylene, we identify three different methyl-cyclopentadiene (c-C₅H₆) isomers (Fig. 3a, left trace), which are prototypical PAH precursors together with 3-phenylpropyne, m-methyl-phenylacetylene and indene, and provide valuable clues to soot formation pathways.

To summarize, pyrolysis experiments yield insights into electronic and vibrational spectra and unimolecular decomposition of the xyllyl radicals, which help understand the fuel destruction pathways in xylene flames.[30] This shows that the combination of pyrolysis and flame experiments is a powerful tool to evaluate and develop predictive kinetic models with the goal to make combustion economically and ecologically more viable.

Catalysis

In addition to more efficient combustion thanks to advanced engineering concepts and predictive kinetic models, the use of sustainable and CO₂-neutral fuels is a further approach to mitigate the environmental cost of energy production. Catalytic fast pyrolysis (CFP) of biomass, e.g. waste plant material, stands out as one of the most promising techniques.[32] Besides cellulose and hemicellulose, lignin is the third major component in biomass, containing phenolic, alkynloxy and arylxylo subunits. This makes it ideally suited for the production of gasoline and valuable precursors for the chemical and pharmaceutical industry.[33] Efficient lignin depolymerization and deoxygenation techniques, e.g. by catalytic fast pyrolysis (CFP), would therefore be of value.[34] The first step involves depolymerizing the lignin macromolecule to phenolic subunits, such as guaiacol (2-methoxyphenol). They are then further pyrolyzed on porous zeolite catalysts. CFP has only been tested in a few pilot-plants,[35] and the technical difficulties had been underestimated, in part because the fundamental chemical processes are not fully understood. This often results in low selectivity and unsatisfactory conversion.

We think that identifying the reactive intermediates and understanding the reaction mechanisms are key to optimizing these processes, especially if ‘cook-and-look’ strategies fail. Guaiacol represents most of the functionalities in lignin and thus serves as model compound.[78] The underlying chemistry on the catalyst surface can be resolved by sensitive and isomer-specific detection of elusive species. Surface intermediates are difficult to identify in situ due to spectral congestion and, even if they are desorbed from the surface to some extent, standard chemical analysis tools, e.g. gas chromatography and coupled with mass spectrometry (GC/MS) are too slow to identify them due to rapid quenching prior to detection.

We have developed a novel system, which combines a catalytic reactor (see Fig. 4a) with the PEPICO detection technique (py-iPEPICO). Guaiacol was highly diluted in an inert carrier gas (Ar) and pulsed into a zeolite-catalyst (HUSY) coated quartz glass reactor held at 400–500 °C. The products and intermediates desorbed from the catalyst surface are ionized using VUV radiation and detected by PEPICO. Due to the low pressure (<0.5 mbar) in the reactor and fast expansion into high vacuum, gas-phase reactive intermediates are preserved and detected. In addition to unveiling the mechanism based on the isomer-specific identification of the desorbed species, time-on-stream (tos) curves can also be recorded by py-iPEPICO and yield insights into the temporal evolution of the state of the catalyst, its activity and the desorption processes. This approach introduces a pressure gap to ambient pressure CFP. To bridge it, we have also conducted experiments in a commercial pyrolysis gas chromatography mass spectrometry setup (py-GC/MS, see Fig. 4b) and observed the same stable reaction products: phenol (m/z = 94, 21), anisole (23, m/z = 108) and cresols (22, methyl-phenols, m/z = 108) in both setups. However, the intermediates fulvene (13, m/z = 92), (methyl)-cyclopentadiene (16 and 17 at m/z = 66 and 80) and fulvone (18, m/z = 78) were only observed in the py-iPEPICO setup (see Scheme 2). While benzene (19) was found as the sole C₆H₆ isomer in the py-GC/MS experiments, we also identified fulvene (c-C₅H₆=CH=), 18 at m/z = 78 in the py-iPEPICO setup. This confirms fulvone as the reactive intermediate upon benzene formation, as speculated previously in the literature.[37]

Based on the py-iPEPICO results, we can establish the reaction mechanism of the zeolite-catalyzed fast pyrolysis of guaiacol as summarized in Scheme 2: After demethylation of guaiacol (11, m/z = 124), catechol (12, 1,2-benzenediol, m/z = 108) is formed in a transmethylation reaction. Transmethylation can be suppressed by pyrolyzing pure catechol, in which case CO₂, CO, phenol (21), cyclopentadiene (16) and fulvenone (13) were only observed, as seen in the tos curve in Fig. 4c. The central intermediate fulvenone (13) is formed in a Bronsted acid catalyzed dehydration reaction (12 → 13), as evidenced by the suppression of fulvenone in the absence of Bronsted acid sites on the catalyst. We also found that hydroxide/hydrogen transfer reactions from coke or highly condensed polyaromatics (produced as side products upon CFP) are responsible for the formation of phenol (21) and cyclopentadiene.
(16) from fulvenone. The phenoxy radical (15) is formed after hydrogen atom addition to fulvenone and is stabilized by a second hydrogen transfer to yield phenol. Alternatively, the C\textsubscript{18}H\textsubscript{16} adduct loses CO to form cyclopentadienyl (14, c-C\textsubscript{5}H\textsubscript{4}) and stabilizes to yield cyclopentadiene (16). Fulvenone was thus found to be the missing central reactive intermediate in the deoxygenation reaction of lignin model compounds.\cite{108} This reaction is essential to upgrading lignin to fuel and gasoline, where a low oxygen content is generally imperative. Furthermore, \textsuperscript{13}C-labeling of the methoxy functionality of guaiacol (11, see orange asterisk in Scheme 2) helped to follow the fate of the methyl group and to complete the reaction mechanism. Benzene can be formed either by methylation of cyclopentadiene (16) over fulvene (18) or by dehydration of phenol (21 \rightarrow 19). Transmethylation is responsible for cresols (22), anisole (21) and methyl-cyclopentadiene (17) formation.

Although guaiacol is a comparatively small molecule, it already follows a complex chemistry upon CFP, and we believe that the detailed understanding of these mechanisms is needed to optimize this process for large-scale industrial use. Our technique can provide valuable insights into reaction mechanisms in heterogeneous catalysis and constitutes an excellent extension to surface sensitive detection methods.\cite{102,73}

**Conclusion**

Reactive intermediates drive chemical reactions in combustion processes and in heterogeneous catalysis. Identifying them amounts to unveiling the reaction mechanism. In this work, we show by using a combination of mass spectrometry and photoelectron spectroscopy with VUV radiation that elusive species can be iso-mer-selectively detected in the gas phase. Such an approach helped establish the unimolecular decay mechanism of \(\alpha\)-xylyl radicals in pyrolysis reactors to form \(\text{e.g.}\) \(\alpha\)-xyylene at low temperatures and styrene at elevated ones. Second, these insights could be called upon in rationalizing model flame experiments, in which the \(m\)-xylyl mole fraction was found to be much below the value predicted by models in which the isomerization channel is not included. We argue that such observations will help develop and improve predictive combustion models. Third, studying the gas phase fraction desorbed from the catalyst surface in the catalytic fast pyrolysis of guaiacol by py-PEPICO revealed fulvenone ketene as the central reactive intermediate in the deoxygenation reaction. Control experiments without a mobile methyl group, isotope labeling and \(\text{Brønsted acid site suppres-}

**Acknowledgements**

We acknowledge funding by the Swiss Federal Office of Energy (BFE) under contract number SJ/501269-01, and thank Patrick Ascher for technical support. Experiments were carried out at the VUV beamline at Swiss Light Source, Paul Scherrer Institute. We are grateful to Dr. Markus Köhler and Thomas Bierkandt for providing the photo of the flame (Fig. 3b) and the experimental data (Fig. 3c).

Received: January 24, 2018

---

**Scheme 2. Reaction mechanism of the catalytic fast pyrolysis of guaiacol over a HUSY zeolite catalyst.**

**Fig. 4. Mass spectra of the catalytic fast pyrolysis of guaiacol in a) our py-PEPICO setup and b) in a conventional pyrolysis gas chromatography/mass spectrometry setup (py-GC/MS). While both setups yield the same final products, we identify lighter and more reactive species in the py-iPEPICO setup exclusively. A time-on-stream curve (c) shows time-dependent traces of intermediates and products of a pure catechol sample over an HUSY zeolite catalyst.**
