

Probing pyrolytic PAH chemistry in high-repetition-rate shock tube coupled to synchrotron-based double imaging photoelectron/photoion coincidence spectroscopy

Fabian E. Cano Ardila¹, Sharath Nagaraju¹, Robert S. Tranter², S. Abid¹, Anthony Desclaux¹, Anthony Roque Ccacya¹, Nabiha Chaumeix¹, Andrea Comandini¹

¹Institut de Combustion, Aérothermique, Réactivité et Environnement, CNRS-INSIS UPR-3021, Orléans, France

²Chemical Sciences and Engineering Department, Argonne National Laboratory, Illinois USA

1 Introduction

Recent innovative techniques for kinetic studies include the design of miniature high-repetition-rate shock tubes (HRRSTs) for use at Synchrotron facilities [1] which make it feasible to study high temperature and pressure chemistry using the most advanced available diagnostic techniques. In particular, a recent investigation on ethanol pyrolysis has demonstrated the potential of coupling the ICARE-HRRST to the synchrotron-based double imaging photoelectron/photoion coincidence spectroscopy (i²PEPICO) [2] at the beamline DESIRS of SOLEIL. i²PEPICO technique provides not only high-resolution mass spectra but also the photoelectron spectra (PES) of the species. This is particularly attractive when complex mixtures of PAH compounds need to be studied.

The aim of the present work is to present the results of the first pyrolytic study on aromatic chemistry performed with the HRRST/i²PEPICO techniques, and to illustrate the capabilities of such techniques in relation to the PAH formation chemistry. For this purpose, toluene was chosen as a fuel due to its relevance as a fuel surrogate component and as intermediate for the PAH appearance and growth. This study complements the literature works on the kinetics of toluene pyrolysis, which includes, among the others, speciation studies using conventional high-pressure shock tube techniques [3,4] and atmospheric and sub-atmospheric flow reactors [5,6]. In particular, the HRRST/i²PEPICO coupling may be used to overcome some of the limitations in the conventional shock tube / gas chromatography techniques, such as condensation of heavy compounds and lack of isomer specificity.

2 Experimental set-up

The detailed description of the functioning and performances of the ICARE high-repetition-rate shock tube and the i²PEPICO technique as implemented at the beamline DESIRS of the Synchrotron SOLEIL has been reported in previous publications [2,7]. Here only some details related to the coupling between the two instruments are reported. The last portion of the HRRST 8 mm i.d. driven section, which contains the end-wall with the nozzle, the four venting valves, and two 60 mm sections, is inserted inside the

primary vacuum chamber (SAPHIRS) and sustained on rails which allows easy mounting and dismounting. The vacuum level inside SAPHIRS during operation is between 10^{-6} and 10^{-3} mbar. The fill valve and the high-pressure solenoid valve are placed just outside the vacuum chamber. The interface between the inside and the outside of SAPHIRS is made through an 8 mm i.d. tube and a bellow which allows the shock tube to move as necessary for alignment purposes. Indeed, the chamber where the HRRST sits can be mechanically moved to guarantee the alignment between the two skimmers which form the double stage pumping system. On the other hand, the alignment between the HRRST nozzle and the first skimmer is obtained by means of a “cage” attached to the skimmer holder. The end of the cage is machined to accept the end-section of the miniature shock tube. The concentricity of the parts is < 0.01 mm and thus axial alignment of the nozzle and the skimmer is ensured. Compared to the previous design, the new cage allows the distance between the nozzle tip and the skimmer tip to be easily varied. With the first and second skimmer orifices equal to 1 and 2 mm respectively, and with a nozzle orifice of 400 μm , the optimal distance between the nozzle and the skimmer tips is found to be around 9.5 mm. This distance allows the pressure inside the mass spectrometer chamber to remain at acceptable levels even when the shock tube runs at 1.5 Hz (between 10^{-8} and 10^{-6} mbar during operation). Despite this, all the experiments presented here are performed at 1 Hz repetition rate.

Two different modes of operation concerning the data acquisition from the DELICIOUS mass spectrometer were implemented. The first is identical to the mode used in ref. [2], where for each HRRST run a trigger signal is sent to the mass spectrometer control computer which acquires data for an 8 ms time span (“pulsed mode”). Each run is associated with specific ions/electrons arriving at the detectors as function of time, thus the kinetics can be extracted from the raw data. On the other hand, as also noticed in [2], due to the specific pulsed character of the HRRST operation accurate PES curves can be obtained only for species with relatively high concentrations. In order to overcome this limitation, a second mode of acquisition was tested (“continuous mode”). In this case, the data are continuously saved and averaged, so that higher signals could be obtained. Of course, there is no possibility to have kinetic information in this second mode. In particular, the pulsed mode was used with photon energy of 10 eV, so that the fuel as well as the main aromatic intermediates could be measured, while the work in continuous mode with photon energy of 8.5 eV, thus focusing specifically on the PAH species. More than 110 633 experiments were averaged in the pulsed mode, while around 46 542 in continuous mode. All the experiments were performed with mixtures composed of 0.1% toluene in argon bath gas. The average temperature and pressure conditions behind the reflected shock wave are $T_5=1488 \pm 18$ K and $P_5=7.6 \pm 0.1$ bar, respectively.

3 Results and discussion

The experimental results are shown in the Figures (1-4). The i²PEPICO data are complex matrices of ion/electron events as function of the position on the detectors and of time, and they can be used to obtain various information, including mass spectra. The mass spectrum obtained from the pulsed mode is presented in Figure 1. This takes into account the contribution of molecules coming at pre-shock conditions, reflected conditions and after the arrival of the rarefaction wave, during a period of time of 8 ms. The mass spectrum has been divided into four regions for better visualization. Starting from the big peaks, at small mass to charge ratio of m/z 40 we can see the second order harmonic of argon, followed by peaks corresponding to the one ring molecules. For previous work using gas chromatography we could measure toluene, the fuel, and largest product benzene, which is produced from toluene pyrolysis through the ipso-substitution reaction “ $\text{C}_7\text{H}_8 + \text{H} = \text{C}_6\text{H}_6 + \text{CH}_3$ ”[4]. Similarly, in the present study m/z 78 and m/z 92 are the biggest peaks corresponding to toluene and benzene. Also, in our laboratory-based work [4] large amounts of phenylacetylene and styrene were measured which are confirmed here at m/z 102 and m/z 104, respectively, plus an small amount of ethylbenzene as a minor single first ring (m/z 106). It is interesting that in the present mass spectra the resonantly stabilized benzyl radical is measured at m/z 91. Smaller non-aromatic species like for instance m/z 52 and m/z 74 are detected, which corresponds to isomers of C_4H_4 and C_6H_2 . Concerning larger PAH molecules,

between two and three rings, the gas chromatographic measurements showed some major products including indene (m/z 116), naphthalene (m/z 128), acenaphthylene (m/z 152), fluorene (m/z 166), phenanthrene/anthracene (m/z 178), and of course bibenzyl from the benzyl recombination (m/z 182) with the presence also of minor isomers like 1-methylene indene (m/z 128) and 1-ethylnaphthalene (m/z 152). These compounds are also the major peak in the mass spectra in Figure 1, confirming the importance of the related kinetic pathways. The data obtained with the pulsed mode may be used to obtain the photoelectron spectra for isomer identification but a more efficient way involving the data acquisition in continuous mode will be presented in the second part of the manuscript, with improved signal to noise ratio for better characterization of the photoelectron spectra. In addition to the major species in common with the previous GC work, other masses are here present for two and three ring minor species, including m/z 168 (biphenylmethane the most probable isomer), and m/z 115 and m/z 165 which should correspond to indenyl and fluorenyl radicals, respectively. Other smaller peaks include m/z 126, m/z 140, m/z 142, m/z 176 and m/z 180. The correspondence of the m/z 154 with acenaphthene/biphenyl needs to be confirmed based on the PES.

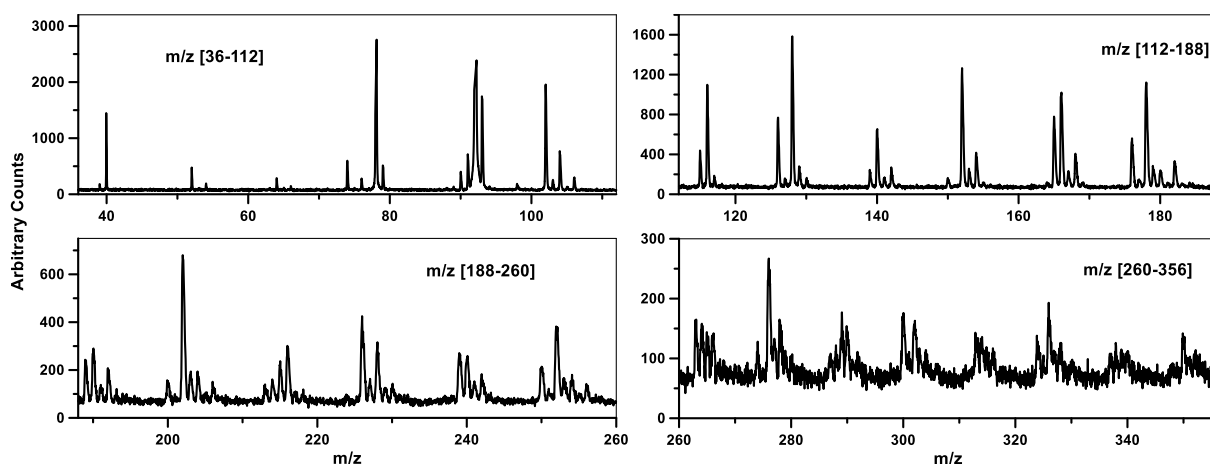


Figure 1. Mass spectrum obtained in pulsed mode, averaging over 110 633 experiments. 0.1% toluene in argon, photon energy 10 eV.

For larger PAHs, m/z 202 is the major product and it corresponds to four rings products (pyrene and fluoranthene, as also shown in our previous work [4]) that are going to be analyzed in the second part with more detail using the PES. From the mass spectra, one can see also clearly defined peaks corresponding to four to five ring species that are larger than what can be achieved in our GC-based system like m/z 190, m/z 216, m/z 226, m/z 228, m/z 240, m/z 250, m/z 252 and m/z 280. The species identification for these peaks needs to be confirmed. Bigger species than these are also visible but with low signal levels as can be seen in the mass spectrum. Additional experiments would have been necessary to increase the definition of the peaks for these large molecular weight species.

The raw i²PEPICO data can be also used to derive the kinetics of the fuel and products as in Figure 2. In the toluene (m/z 92) concentration profile, initially the concentration corresponds to the fresh gases before the arrival of the shock, then a step increase around 1300 μ s corresponding to reflected conditions. Once the mixture is at shocked conditions, the concentration of toluene decreases slowly as the fuel is pyrolyzed and finally around 1800 μ s, a steep decrease is observed. One of the main products also plotted, benzene (m/z 78), is formed after a certain delay, it reaches a maximum at around 2000 μ s and then it is consumed at a slower rate. Based on temporal profiles of toluene and benzene, one would question if these profiles are not impacted by the pressure history during the observation time. Indeed, behind the reflect shock wave there is an increase of the pressure during around 500 μ s, until the arrival of the rarefaction wave, then a decrease of the pressure, that lasts around 500 μ s, due to the rarefaction waves [2]. In order to identify if the pressure history has an impact on the species profiles, experiments were performed, in the same conditions, using 1% CO₂ in argon monitoring the CO₂ profile: during the

1 ms, no drop in the CO₂ profile was observed indicating that the results are not impacted by fluid dynamics in the shock tube.

Additionally to benzene, temporal profiles for the PAHs were measured. This is exemplified in Figure 2, which illustrates the temporal profiles for *m/z* 128 and *m/z* 116: after a delay of around 500 μ s, they start forming at 1800 μ s, after reaching a maximum, the concentrations decrease. Larger molecules like *m/z* 202 start forming at later times, around 1900 μ s considering the kinetic profiles.

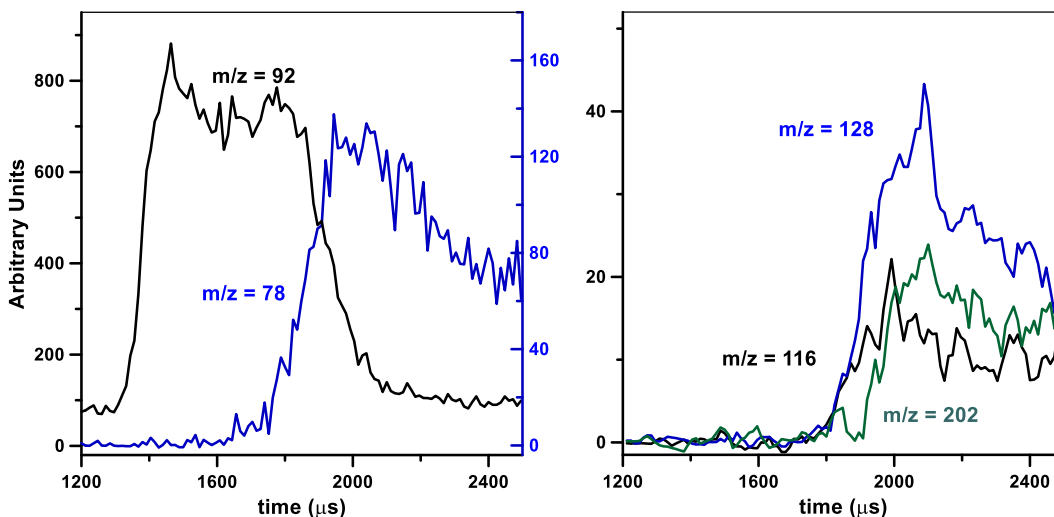


Figure 2. Kinetics for selected species. 0.1% toluene in argon, photon energy 10 eV.

A second series of runs have been carried out in the continuous mode to obtain the photoelectron spectra which are very useful to identify isomers at a given *m/z*. These experiments are less demanding regarding the averaging, for example, "only" 46 542 runs were needed instead of more than 100 000 runs in the previous case. The mass spectra, for an ionization energy fixed at 8.5 eV are illustrated in Figure 3. As one can see the mass spectrum is very different from the one at 10 eV and it is focused on PAHs *m/z*.

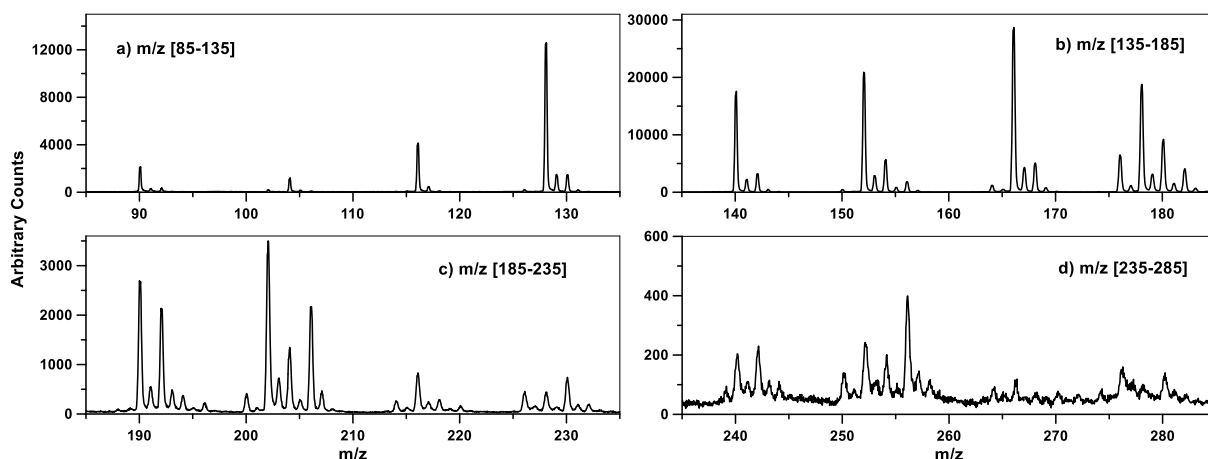


Figure 3. Mass spectrum obtained in continuous mode, averaging around 46 542 experiments. 0.1% toluene in argon, photon energy 8.5 eV.

The advantage of investigation the photoelectron spectra is to identify an *m/z* the different isomers when their PESs are known. For example, Figure 4 reports the experimental PES measured in this work and the PES from the literature for the same *m/z*. At *m/z* 128, the experimental curve (black line) exhibits several well-defined peaks which corresponds to the literature PES for naphthalene [8]. In fact, the PES of 1,2,3-metheno-1H-indene,2,3-dihydro [9] shows a wide peak which is not observed in our

measurements. These two isomers are the ones for which it was possible to find literature experimental PESs, future calculations and experiments are required to obtain PESs for additional isomers. At m/z 202, the comparison with the available PESs clearly shows the contribution to the overall signal from pyrene [10] (blue line), while the PES of fluoranthene [11] (green line) and 9-ethynyl-phenanthrene [11] (orange line) are very similar, and the related contributions cannot easily be separated. On the other hand, it is possible to exclude 1,1'-biphenyl,2,2'-diethynyl- [12] (brown line) from the isomers present in the mixture. There are other possible isomers, but the lack of PESs data in the literature did not allow their identification.

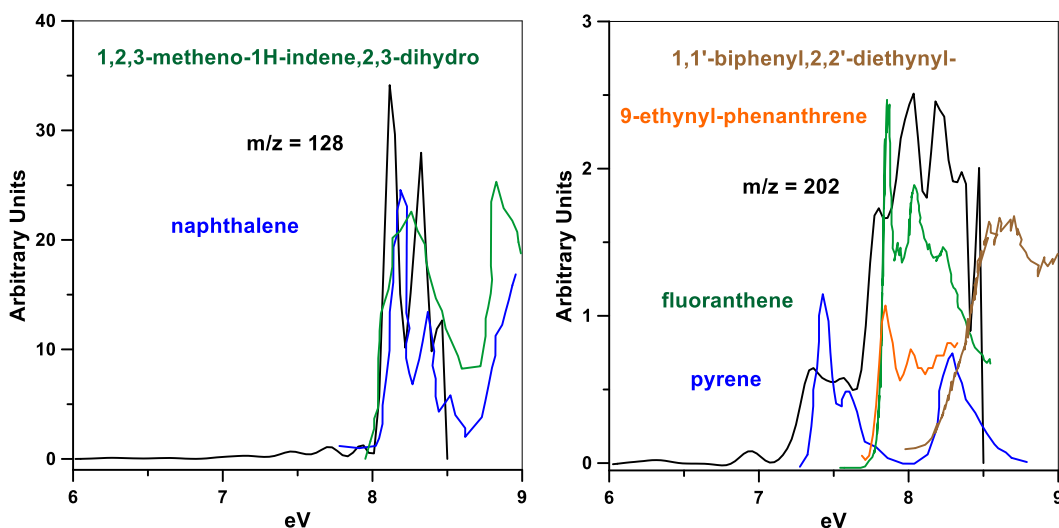


Figure 4. Photoelectron spectra for m/z 128 and m/z 202 (experimental), naphthalene [8], 1,2,3-metheno-1H-indene,2,3-dihydro [9], pyrene [10], fluoranthene [11], 9-ethynyl-phenanthrene [11], 1,1'-biphenyl,2,2'-diethynyl- [12]. Photon energy 8.5 eV.

4 Conclusions

In the present work, results of the first pyrolytic study on aromatic chemistry performed with the HRRST/i²PEPICO techniques are presented. These new results illustrate the capabilities of such techniques in relation to the PAH formation chemistry that cannot be achieved with regular analytic studies in the laboratory (shock tube coupled to GS-MS). In this work, are reported the decomposition of 0.1% toluene in argon at an average temperature and pressure of 1488 K and 7.6 bar respectively. Two different series of experiments have been performed: (i) with pulsed mode (reflected shock time identified) with more than 100 000 runs and (ii) continuous mode with more than 40 000 runs. Well defined mass spectra and the evolution of the species profiles during the pyrolysis of toluene have been obtained (from light species up to 5-member rings) in the pulsed mode at an ionization level of 10 eV. In the continuous mode, at an ionization level of 8.5 eV, photoelectron spectra were obtained for some PAHs which allowed the identification of isomers which could not have been done without i²PEPICO. This work also exemplifies the need of high repetition rate shock tubes to perform such studies.

Acknowledgements

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement N° 756785). We are grateful to the whole SOLEIL staff for provision of beamtime under project 20190102, in particular to Dr. Nahon and Dr. Garcia for the support to the experiments. Robert Simon Tranter acknowledge support

from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences through Argonne National Laboratory and the Argonne Sandia Consortium on High Pressure Combustion Chemistry. Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC, under contract DE-AC02-06CH11357

References

- [1] Tranter RS, Lynch PT. (2013). A miniature high repetition rate shock tube, *Rev. Sci. Instrum.* 84: 094102.
- [2] Nagaraju S, Tranter RS, Cano Ardila FE, Abid S, Lynch PT, Garcia GA, Gil J-F, Nahon L, Chaumeix N, Comandini A. (2021) *Comb. Flame* 226: 53.
- [3] Sivaramakrishnan R, Tranter RS, Brezinsky K. (2006). High pressure pyrolysis of toluene. 1. Experiments and modeling of toluene decomposition, *J. Phys. Chem. A* 110: 9388.
- [4] Sun W, Hamadi A, Abid S, Chaumeix N, Comandini A. (2020). Probing PAH formation chemical kinetics from benzene and toluene pyrolysis in a single-pulse shock tube, *Proc. Combust. Inst.* 38: 891.
- [5] Shukla B, Susa A, Miyoshi A, Koshi M. (2007). In situ direct sampling mass spectrometric study on formation of polycyclic aromatic hydrocarbons in toluene pyrolysis, *J. Phys. Chem. A* 111: 8308.
- [6] Yuan W, Li Y, Dagaut P, Yang J, Qi F. (2015). Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. I. Flow reactor pyrolysis and jet stirred reactor oxidation, *Combust. Flame* 162: 3.
- [7] Garcia GA, Cunha de Miranda BK, Tia M, Daly S, Nahon L. (2013). DELICIOUS III: a multipurpose double imaging particle coincidence spectrometer for gas phase vacuum ultraviolet photodynamics studies. *Rev. Sci. Instrum.* 84: 053112.
- [8] Eland JHD, Danby CJ. (1968). Inner ionization potentials of aromatic compounds, *Zeitschrift für Naturforschung A*, 23: 355.
- [9] Gleiter R, Gubernator K, Eckert-Maksic M, Spanget-Larsen J, Bianco B, Gandillon G, Berger U. (1981). The electronic structure of phenylene and naphthylene bicyclobutanes. Photoelectron spectroscopy and model calculations, *Helv. Chim. Acta*, 64: 1312.
- [10] Mishra PM, Avaldi L, Bolognesi P, Prince KC, Richter R, Kadhane UR. (2014). Valence Shell Photoelectron Spectroscopy of Pyrene and Fluorene: Photon Energy Dependence in the Far-Ultraviolet Region, *J. Phys. Chem. A* 118: 3128.
- [11] Mercier X, Faccinetto A, Batut S, Vanhove G, Božanić DK, Hróðmarsson HR, Garcia GA, Nahon L. (2020). Selective identification of cyclopentaring-fused PAHs and side-substituted PAHs in a low pressure premixed sooting flame by photoelectron photoion coincidence spectroscopy. *Phys. Chem. Chem. Phys.* 22: 15926.
- [12] Gleiter R, Schafer W, Eckert-Maksic M. (1981). Transannulare Wechselwirkungen zwischen Acetylenen - Photoelektronenspektroskopische Untersuchungen an 1,8-Diethylnaphthalin und cyclischen Derivaten von 2,2'-Diethylnbiphenyl, *Chem. Ber.* 114: 2309.