TIME RESOLVED MONITORING OF CHLOROAROMATICS FROM A 'DE NOVO' REACTION BY JET-REMPI MASS SPECTROMETRY

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Introduction

The propensity of fly ashes from refuse incinerators to form dioxins and related compounds in a narrow temperature window around 300 °C, the so-called ´de novo' formation, is known since the pioneering work of Stieglitz and coworkers, see e.g.[1]. The same ability was observed for filter dust from iron ore sintering and other metallurgical processes as well[2].

To study the de novo formation in more detail a laboratory flow reactor containing sintering belt ESP fly ash was coupled to a REMPI (resonant enhanced multiphoton ionization) mass spectro-meter. The idea at the start was to measure as many volatile chloroaromatic compounds as possible, as a function of reactor temperature and other experimental parameters, to assess their role either as precursors or as products formed in de novo parallel processes and establish any shift in congener distribution relevant to the mechanisms in dioxin formation. In addition, the time dependence was to be monitored, although on the basis of earlier conventional measurements only a moderate time effect was anticipated.

However, a strong time dependence of the released aromatic compounds was established. This forced us to abandon our normal measurement strategy using isolated states (see below). Consequently, mostly uncalibrated profiles were obtained, but nevertheless new insight into the de novo synthesis, more in particular a sequential formation of chlorinated compounds can be derived.

Methods

Our REMPI apparatus has been described in detail in the literature, see e.g.[3]. In the context of this paper it is important to distinguish between the two methods of ionization compared in Fig.1. Generally, in a two-photon ionization process, target molecules are excited upon absorption of a first photon. Subsequent absorption of a second photon leads to ionisation. When low-lying states are used for excitation, as shown on the left-hand side of Fig.1, one has to deal with widely separated (isolated) states. This requires the laser to be tuned to provide photons of the desired energy and, in conjunction with sample cooling, this allows selectively ionizing different molecules by an appropriate choice of the photon energy and thus to discriminate between isomers.

When higher states are used for excitation (right-hand side) the situation is entirely different as these states are very close to each other and quite often overlap. As a result wavelength-selectivity is mostly lost and even fixed-frequency lasers can be used, as nearly always a resonant state is met. Another advantage of this simplified method is that many compounds can be measured simultaneously, provided that they possess states at the selected irradiated photon energy.

The original plan for this work was to perform complete wavelength scans of the product mixtures emanating from the reactor resulting in ion signals as a function of wavelength and for different masses, i.e. a 3D plot. This would have allowed selecting a series of target compounds, along with the respective wavelengths suitable for their efficient ionization. It was found, however, that the mixture

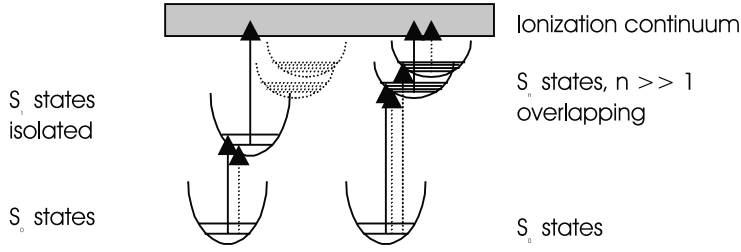


Figure 1. Alternative variants of resonant two-photon ionization

behind the reactor changed so rapidly that a wavelength scan even over a reduced range was impossible. Consequently, we changed our strategy and only measured 5 compounds via low lying excited states (left-hand side of Fig.1) by using resonant wavelengths known from previous work[4]. For this purpose the tunable laser was automatically switched from one wavelength to the next, normally within a couple of seconds. These compounds and their respective wavelengths are benzene or Bz (258.8 nm), toluene (266.9 nm), ClBz (269.8 nm), DiClBz (272.6 nm), phenol (274.9 nm). In addition, benzofuran, dibenzofuran and naphthalene could be measured at 258.8 nm. For these compounds calibration was performed by comparison to standard mixtures.

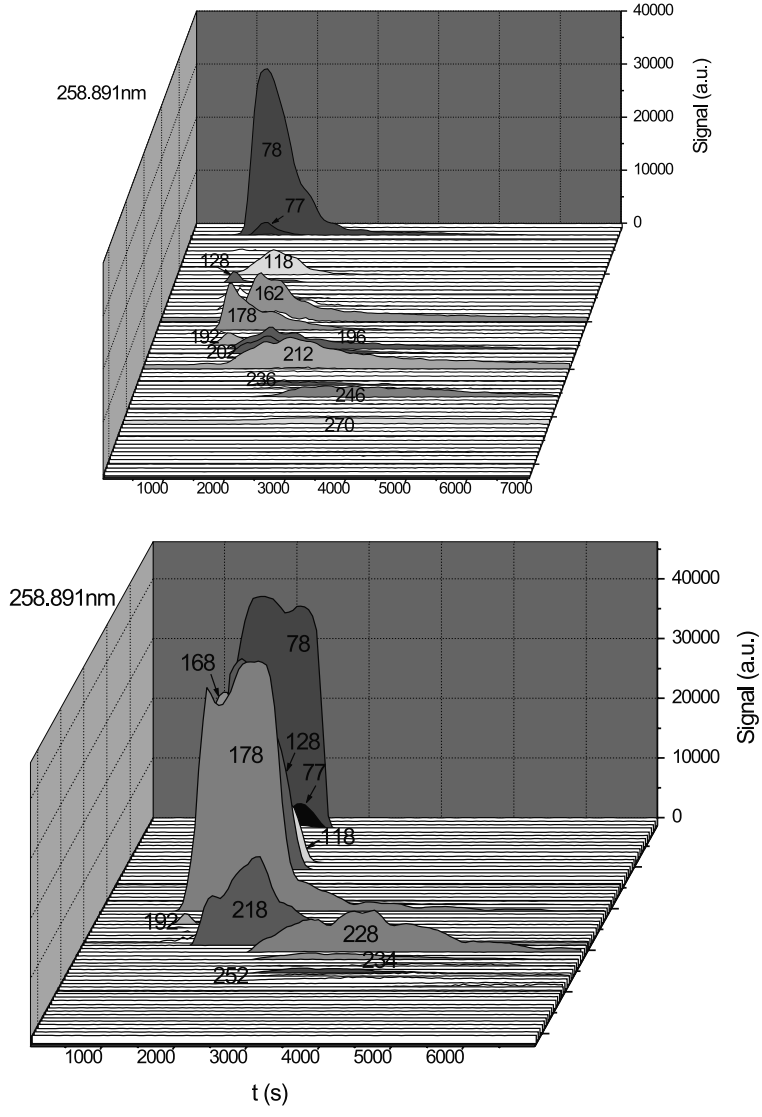
It was found, that the wavelength for selective benzene ionization (258.8 nm) provides sufficient energy to ionize higher aromatics via higher states (right-hand side of Fig.1). As a result, many other compounds along with their methylated and chlorinated homologues could be measured at this wavelength and these data are analysed in this and next papers. Due to a lack of wavelength selectivity, mass spectrometric interferences could never be excluded. As a guide for peak identification, it was attempted to plot series of homologues. Although the signals are not calibrated these sets show an interesting sequential behavior with regard to chlorination.

Results and discussion

Two of these measurements are shown in Figs.2 and 3. In Fig.2 the resonantly measured Bz signal is the main peak and it disappears altogether after ca. 2000 s. The same holds for benzofuran BzF (118 amu). Monochloronaphthalene MCN (162), by contrast, develops a considerable tail. Similar behaviour is also found for the pair phenanthrene Phen (178) and monochlorophenanthrene MCPhen (212). Polychlorinated peaks start only after a distinct delay and show an even stronger tail, e.g. dichlorodibenzofuran DCDF (236) or dichlorophenantrene DCPhen (246). It can thus be concluded that the generation of chlorinated compounds is delayed with respect to that of their non-chlorinated parent structures. The following sequence seems to apply: “Benzene, naphthalene, and other aromatics form first, followed by monochlorinated products, such as chlorobenzene and chloronaphthalene, and later also by di-, tri-, tetra-, … chlorinated products. However, in order to discriminate between various possible hypotheses the signal curves have been investigated in detail and the results of this analysis is discussed in an associated paper. A third paper relates to an experiment featuring stepwise rises of the reaction temperature.

The signals of Fig.3 (350 °C) were recorded with a smaller gain (factor 3). Nevertheless, Bz and in particular phenanthrene (178) as well as most other large peaks are saturated, i.e. the emissions are significantly higher than the signal suggests. One observes again that non-chlorinated compounds are emitted in the early phases of the process only, followed by mono- and polychlorinated compounds. Entirely new is the 228 amu signal belonging to a structure with 4 condensed aromatic rings, attributed

to benzophenanthrene as the weak 226 signal and Benzo(ghi)fluoranthene, Fig.4 show exactly the same time dependence.



Figures 2 and 3. Concentration profiles of major species at 300 °C (top) and 350 °C (bottom).

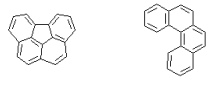


Figure 4. Structures of Benzo(c)phenanthrene and of of Fluoroanthene

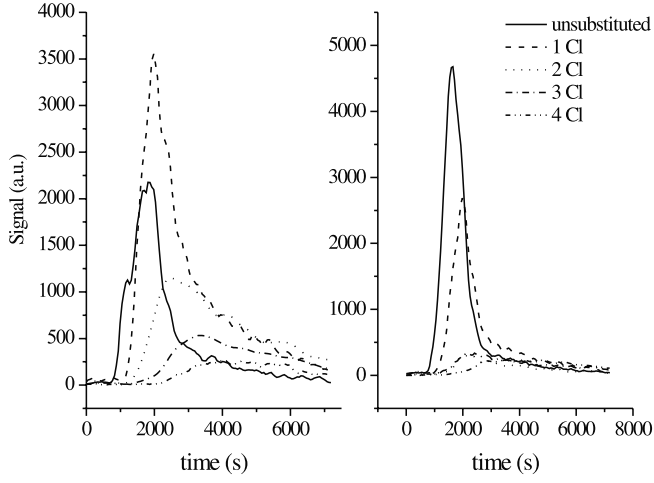


Figure 5. Sequential chlorination of dibenzofurans (left) and benzofurans (right) measured at 300 °C.

Finally, in Fig.5 two typical examples for sequential chlorination are shown, also observed for all other homologue sets. For the set of benzofurans no major mass spectrometric interference is to be expected. In the case of the furan set, however, one has to consider the pyrene series as well, since pyrene interferes with MCDF, monochloropyrene with DCDF etc. This is obviously a limitation of the non-selective ionisation method used in this study. To some extent making use of the Cl isotope distributions can disentangle such interferences, but this exercise is still stored for future study. In general, one can say that this work is by no means complete. Nevertheless, it is obvious that time resolved measurements will facilitate future mechanistic interpretations and for the first time have permitted to analyse the initial stages and sequential evolution of the de novo synthesis.

Acknowledgement

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