Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI)

to

Influences of the molecular fuel structure on combustion reactions towards soot precursors in selected alkane and alkene flames

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1. Available data files

The following files are available as supplemental data in .txt format for the *n*-pentane (**ESI_2**), 1-pentene (**ESI_3**) and 2-methyl-2-butene (**ESI_4**) flames:

- **ESI_2** (*n*-pentane) includes experimental main and intermediate species mole fraction profiles measured with EI-MBMS.
- **ESI_3** (1-pentene) includes experimental main and intermediate species mole fraction profiles measured with EI- and PI-MBMS.
- **ESI_4** (2-methyl-2-butene) includes experimental main and intermediate species mole fraction profiles measured with EI- and PI-MBMS.

All data refer to the flame conditions presented in the paper.

2. Data evaluation procedure

For EI- and PI-MBMS experiments the integrated, energy-dependent ion signal of a species *i* is linked to its mole fraction x_i by the following equation:

$$S_i(E) = x_i \cdot SW \cdot \varphi \cdot D(M_i) \cdot c \cdot FKT(T) \cdot \int \sigma_i(\tau) \cdot f(E-\tau)d\tau \qquad (1)$$

where *SW* is the number of time-of-flight mass spectra recorded and summed at each data point, φ the number of photons or electrons involved in the ionisation process and $D(M_i)$ the mass discrimination factor of species *i*, which was determined using cold gas measurements of standard calibration gases and the method described by Cool *et al.* [1]. *FKT* denotes a temperature dependent sampling function and *c* an instrument parameter. Based on the assumption that the instrument parameter *c* was constant for all scans, the product of both variables was obtained for the PI-MBMS experiment for each position in the flame using the argon signal (measured at 16.65 eV) and its respective mole fraction adapted from the main species calculation utilising the converted form of Eq. 1 (see Eq. 2).

$$c \cdot FKT(T) = \frac{S_i(E)}{x_i \cdot SW \cdot \varphi \cdot D(M_i) \cdot \int \sigma_i(\tau) \cdot f(E-\tau)d\tau} \quad (2)$$

The integral $\int \sigma_i(\tau) \cdot f(E-\tau)d\tau$ describes the convolution of the energy distribution of ionising particles with the energy dependent ionisation cross section $\sigma_i(E)$ over the entire energy range τ. For PI-MBMS data the integral can be substituted by using tabulated photoionisation cross sections, due to the negligibly small photon energy distribution. As mentioned above, the energy distribution for the EI-MBMS system is much broader and therefore it allows the detection of argon even if the nominal energy of the electrons is below the ionisation energy of argon. Thus, argon can be used always as reference signal for the EI-MBMS and Eq. 1 simplifies to:

$$\frac{S_i}{S_{Ar}} = \frac{x_i \cdot SW \cdot \varphi \cdot D(M_i) \cdot c \cdot FKT(T) \cdot \int \sigma_i(\tau) \cdot f(E-\tau) d\tau}{x_{Ar} \cdot SW \cdot \varphi \cdot D(Ar) \cdot c \cdot FKT(T) \cdot \int \sigma_{Ar}(\tau) \cdot f(E-\tau) d\tau} = \frac{x_i}{x_{Ar}} \cdot k_i(E) \quad (3)$$

with $k_i(E)$ as species- and energy-dependent calibration factor that combines all species-dependent parameters. Referring to argon, only the species-specific calibration factors must be known and the mole fraction x_i of intermediate species can be calculated from the argon mole fraction determined from the main species calculation, which will be explained below.

Generally, the reactants (fuel, O_2), the products (CO, CO_2, H_2O) and the dilution gas argon are considered as main species and their mole fractions were quantified in a similar manner for both – PI- and EI-MBMS – according to Eq. 3 using, whenever possible, a direct calibration method with Ar as reference. Calibration factors of CO and CO_2 ($k_{CO/Ar}$ and $k_{CO2/Ar}$) were determined using standard calibration gases, while those for the reactants ($k_{fuel/Ar}$ and $k_{O2/Ar}$) were calculated based on the flow conditions at the fuel or O_2 burner outlet, assuming that only the respective reactant and argon are present. For the EI-MBMS, the calibration factor of water $k_{H2O/Ar}$ was calculated using a simulated water signal determined through a convolution procedure of the literature ionisation cross section with the known kinetic energy distribution of the ionising electrons (see Schenk *et al.* [2] for details). In the PI-MBMS experiment, the respective H_2O calibration factor as well as the calibration factor for CO were obtained from the respective photoionisation cross section ratios (σ_{H2O}/σ_{Ar} and σ_{CO}/σ_{Ar}). For the determination of the local argon mole fraction profile for each flame position, the balance between the sum of all major species and unity was calculated subsequently. With the known argon mole fraction, intermediate species concentrations are accessible according to Eq. 3 for both experiments using either a literature photoionisation cross section σ_i for PI-, or an energy-dependent and argon-related calibration factor k_i/Ar for EI-MBMS. The latter can be either calculated by a direct calibration method using cold gas measurements of known gas composition, or were estimated by the relative cross section method (RICS)[3], or by a convolution procedure of the literature ionisation cross section with the known kinetic energy distribution of the ionising electrons. The reader is referred to Schenk *et al.* [2] for a detail description of the calibration factor determination in EI-MBMS. Whenever necessary, a fragment correction as well as a correction for the contribution of ^{13}C-isotopes was performed.

3. Mole fraction profiles of the main species

Figure S1 provides the calculated mole fraction profiles of the main species as function of the distance from the fuel outlet for the three different C_5 flames to demonstrate the general reliability of our experimental data and of the data evaluation procedure. The profiles accurately reproduce the typical features of profiles from opposed-flow diffusion flames and the calculated concentrations show reasonable values for all three fuels. Only slight discrepancies between the different fuels are observed. Observable deviations between EI- and PI-MBMS measurements (closed and open symbols, respectively) are within the uncertainty limits of the experiments.

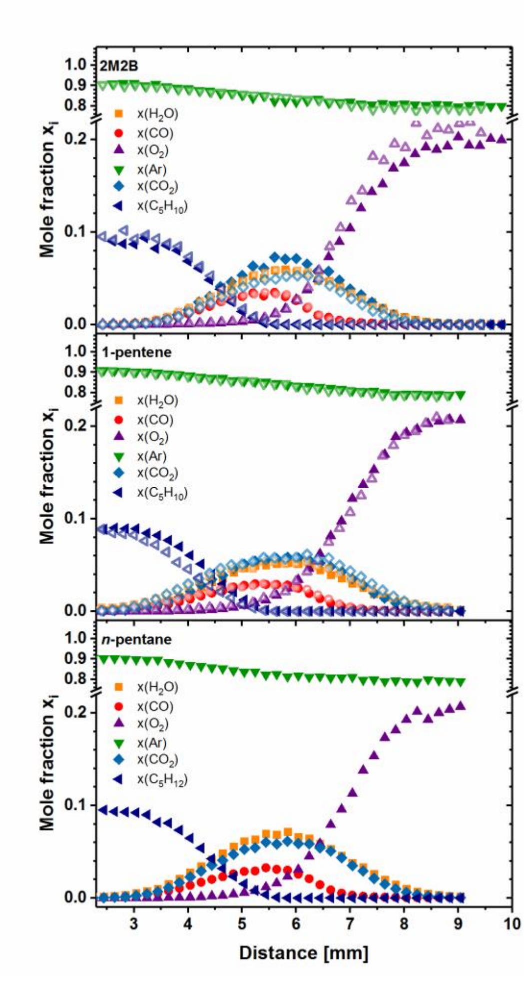

Figure S1: Main species (fuel, O_2, Ar, H_2O, CO, CO_2) mole fraction profiles as a function of the distance from the fuel-outlet for EI- and PI-MBMS measurements (closed and open symbols, respectively).

4. Overview of species concentrations measured with EI- and PI-MBMS

Table S1: Species concentrations measured with EI-MBMS. Maximum mole fractions x_{max} for species with the nominal mass M and the sum formula F at the distance from the fuel-outlet *d* are reported. The scan energy *E* and the calibration method *Cal.* used for the quantification as well as the ionisation energy *IE* are given and the respective literature references are provided. Typical errors depend on the used calibration method. (- : species was not quantified in respective measurement).

				2-Methyl-2-butene				**1-Pentene**				***n*-Pentane**				
M	**F**	**Calibrated as**	***IE***	***E***	***Cal.***	x_{max}	***d***	***E***	***Cal.***	x_{max}	***d***	***E***	***Cal.***	x_{max}	***d***	**Ref.**
/u			***/eV***	***/eV***			***/mm***	***/eV***			***/mm***	***/eV***			***/mm***	
15	CH_3	methyl radical	9.84	-	-	-	-	10.5	RICS (CH_4)	1.9E-05	5.6	12.0	RICS (CH_4)	1.7E-05	5.6	4
16	CH_4	methane	12.61	12.0	direct	4.6E-03	4.6	10.5	direct	9.7E-04	4.4	12.0	direct	1.2E-03	4.8	5
26	C_2H_2	acetylene	11.4	12.0	direct	6.4E-03	5.2	10.5	direct	5.7E-03	4.8	10.5	direct	4.2E-03	5.2	3
28	C_2H_4	ethylene	10.5138	12.0	direct	2.4E-03	5.0	10.5	direct	7.8E-03	4.8	10.5	direct	6.7E-03	4.8	6
30	CH_2O	formaldehyde	10.88	12.0	conv.	3.3E-04	5.6	-	-	-	-	-	-	-	-	7
30	C_2H_6	ethane	11.52	10.5	conv.	7.9E-05	5.4	10.5	conv.	6.2E-04	4.8	10.5	conv.	1.4E-03	5.0	6
39	C_3H_3	propargyl radical	8.67	12.0	RICS (C_3H_4)	3.6E-05	5.0	10.5	RICS (C_3H_4)	5.4E-05	4.8	10.5	RICS (C_3H_4)	1.1E-05	4.6	7
40	C_3H_4	propyne	10.36	12.0	direct	1.4E-03	4.8	10.5	direct	6.4E-04	4.8	10.5	direct	1.8E-04	5.2	7
42	C_2H_2O	ketene	9.617	12.0	conv.	1.8E-04	5.6	10.5	conv.	1.9E-04	5.6	10.5	conv.	1.7E-04	5.6	3
50	C_4H_2	diacetylene	10.17	10.5	conv.	3.5E-04	4.8	-	-	-	-	-	-	-	-	7
52	C_4H_4	vinylacetylene	9.58	12.0	RICS (C_4H_6)	2.8E-04	5.2	10.5	RICS (C_4H_6)	1.3E-04	4.8	10.5	RICS (C_4H_6)	4.5E-05	5.2	7
53	C_4H_5	but-2-yn-1-yl radical	7.95	10.5	conv.	2.0E-05	5.0	-	-	-	-	-	-	-	-	3
54	C_4H_6	1,3-butadiene	9.072	10.5	conv.	1.6E-03	5.0	10.5	direct	8.2E-04	4.8	12.0	direct	4.9E-05	4.8	7
66	C_5H_6	1,3-cyclopentadiene	8.57	12.0	conv.	5.8E-04	5.2	10.5	conv.	1.8E-04	4.8	10.5	conv.	2.7E-05	5.2	3
68	C_5H_8	cyclopentene	9.01	12.0	conv.	5.0E-03	4.8	10.5	conv.	1.6E-04	4.8	10.5	conv.	1.6E-05	4.8	3
78	C_6H_6	benzene	9.24378	10.5	direct	4.7E-04	5.0	10.5	conv.	4.0E-04	4.8	10.5	conv.	6.5E-05	5.2	7
80	C_6H_8	1,3-cyclohexadiene	8.25	10.5	RICS (C_6H_6)	1.4E-04	5.0	10.5	RICS (C_6H_6)	3.1E-05	4.8	10.5	RICS (C_6H_6)	3.9E-06	4.8	3
82	C_6H_{10}	1,3-hexadiene	8.53	10.5	RICS (C_6H_6)	1.3E-04	4.8	10.5	RICS (C_6H_6)	5.4E-06	4.6	12.0	RICS (C_6H_6)	5.8E-07	5.4	3
92	C_7H_8	toluene	8.828	12.0	direct	2.8E-04	5.2	10.5	conv.	9.5E-05	4.8	10.5	conv.	1.4E-05	5.6	3
116	C_9H_8	indene	8.14	12.0	conv.	1.4E-04	5.2	10.5	conv.	2.6E-05	4.8	12.0	conv.	2.3E-06	5.6	3
128	$C_{10}H_8$	naphthalene	8.144	10.5	conv.	4.9E-05	5.2	10.5	conv.	2.3E-05	5.0	10.5	conv.	3.8E-06	5.0	3

Table S2: Species concentrations measured with PI-MBMS in the 2M2B and 1-pentene flame. Maximum mole fractions x_{max} for species with the nominal mass M and the sum formula F at the distance from the fuel-outlet *d* are reported. The photoionisation cross section *σ(E)* and the photon energy *PE* used for the quantification as well as the ionisation energy *IE* are given and the respective literature references are provided. Typical errors depend on the used photoionisation cross section and range up to factors of 2-4 for estimated values.

				2-Methyl-2-butene					**1-Pentene**				
M	**F**	**Calibrated as (for 2M2B/1-**	***IE***	***PE***	***σ(E)***	x_{max}	***d***	**Ref.**	***PE***	***σ(E)***	x_{max}	***d***	**Ref.**
/u			**/eV**	**/eV**	**/Mb**		**/mm**		**/eV**	**/Mb**		**/mm**	
16	CH_4	methane	12.61	14.35	26.78	2.2E-03	5.0	8	13.05	2.32	6.8E-04	5.0	8
26	C_2H_2	acetylene	11.4	11.50	18.26	7.5E-03	5.2	9	11.50	18.26	5.1E-03	4.8	9
28	C_2H_4	ethylene	10.5138	11.50, 10.50	7.92, 0.97	2.6E-03	5.2	10	11.50	7.92	8.2E-03	4.8	10
30	CH_2O	formaldehyde	10.88	11.50	10.13	3.0E-04	5.8	11	11.50	10.13	2.8E-04	5.8	11
30	C_2H_6	ethane	11.52	11.50	4.84	6.3E-05	5.2	12	12.30	11.26	5.2E-04	4.8	12
39	C_3H_3	propargyl radical	8.67	9.50	7.78	5.1E-05	5.6	13	9.00	5.61	1.7E-05	5.8	13
40	C_3H_4	allene	9.692	9.75	0.41	8.0E-04	4.4	14	9.75	0.41	3.6E-04	4.6	14
40	C_3H_4	propyne	10.36	10.50	23.06	1.9E-03	5.2	9	10.50	23.06	5.8E-04	4.8	9
42	C_2H_2O	ketene	9.617	9.75	8.87	2.0E-04	5.8	14	9.75	8.87	1.5E-04	5.4	14
50	C_4H_2	diacetylene	10.17	10.50	23.82	4.3E-04	5.2	14	10.50	23.82	1.5E-04	5.4	14
52	C_4H_4	vinylacetylene	9.58	9.75	13.21	8.4E-04	5.0	14	9.75	13.21	2.4E-04	4.8	14
54	C_4H_6	1,3-butadiene	9.072	9.75	13.59	2.2E-03	5.0	14	9.00	0.17	7.6E-04	4.6	14
64	C_5H_4	1,3-pentadiyne	9.5	10.50	35.00	3.6E-05	4.8	15	10.50	35.00	7.3E-06	5.4	15
65	C_5H_5	cyclopentadienyl radical	8.41	9.50	4.60	3.0E-05	4.8	15	9.50	4.60	3.7E-06	4.2	15
66	C_5H_6	1,3-cyclopentadiene	8.57	9.50	15.67	5.7E-04	5.2	15	9.00	11.65	1.9E-04	4.8	15
68	C_5H_8	2-methyl-1,3-butadiene / 1,3-pentadiene	8.86 / 8.59	10.50	19.00 /	4.2E-03	5.0	16	9.50	12.71	1.6E-04	4.6	14
78	C_6H_6	benzene	9.24378	10.50	31.81	4.9E-04	5.2	14	9.50	11.05	3.0E-04	5.2	14
78	C_6H_6	fulvene	8.36	9.00	14.49	6.8E-05	4.8	17	8.70	7.06	4.4E-06	5.0	17
80	C_6H_8	1,3-cyclohexadiene	8.25	9.50, 9.75	18.39, 24.17	1.3E-04	5.2	18	8.25, 8.70	0.99, 17.57	3.3E-05	5.0	18
82	C_6H_{10}	1,3-hexadiene	8.53	9.25	16.36	1.4E-04	5.2	18	8.70, 9.00	4.39, 12.10	5.3E-06	4.8	18
92	C_7H_8	toluene	8.828	9.25	11.52	3.0E-04	5.0	19	9.00	5.02	1.0E-04	4.8	19
104	C_8H_8	styrene	8.464	9.00	10.36	1.2E-04	4.6	19	8.70	4.04	1.6E-05	5.4	19
106	C_8H_{10}	ethylbenzene	8.77	9.00	6.10	1.4E-04	5.2	19	9.00	6.10	4.2E-05	4.6	19
116	C_9H_8	indene	8.14	9.00	13.60	1.1E-04	5.0	19	9.00	13.60	2.9E-05	4.8	19
118	C_9H_{10}	indane	8.54	9.00, 9.25	8.36, 14.08	4.0E-05	4.8	19	8.70, 9.00	3.37, 8.36	9.8E-06	4.8	19
120	C_9H_{12}	1,3,5-trimethylbenzene	8.4	9.00	12.90	2.4E-05	4.6	19	8.70	7.14	2.6E-06	4.2	19
128	$C_{10}H_8$	naphthalene	8.144	9.50	21.34	6.9E-05	5.4	20	9.00	13.22	2.5E-05	4.6	20
142	$C_{11}H_{10}$	1-methylnaphthalene	7.96	9.00, 9.25	13.93, 19.43	3.5E-05	5.2	19	8.25	5.47	3.7E-06	5.4	19
202	$C_{16}H_{10}$	pyrene	7.426	9.50	55.51	4.4E-06	5.6	21	8.25	14.36	5.3E-07	4.0	21

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