FORMATION AND SOURCES

SEMI-CONTINUOUS JET-REMPI MONITORING OF PCDD/F AND PAH DE NOVO FORMATION. (I) TESTING METHOD AND EFFECT OF TIME

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Introduction

In the frame of the E.U. project MINIDIP the influence of different operating factors was studied[1-2]. This work reproduces some of these tests at FZ- Karlsruhe on the facility used by Dr Hell et al.[1], in which the gas stream from a de novo experiment was analysed after absorbing the products in toluene for typically 2 hours. In this study Jet-REMPI (resonant multiphoton ionization) mass spectrometry is applied allowing a semi-continuous (every 55 s) monitoring, including the initial period of heating the sample. This contribution (I) presents experimental method and data relating to the influence of reaction time and part (II) the effects of temperature on the Jet-REMPI signal. These recent tests throw a new light on the early stages of a de novo reaction experiment.

Materials and methods

12 experiments are conducted using a tubular glass reactor (24.5 mm diameter x 655 mm high) mounted vertically in an oven. A highly reactive dust (5 g) from the second field of the electrostatic precipitator of an iron ore sintering plant is contacted with a flow of dry synthetic air (50 ml/min of 20.5 % O_2 in N_2). The reaction is monitored as a function of time and temperature, with oven settings at 225, 250, 285, 293, and 350 °C. In some tests water vapour is added to the synthetic air, but test results are similar. In a final non-isothermal experiment, starting at 225 °C, the set temperature is stepwise increased, adding 25 °C every 15 minutes until 350 °C (see part II). The data was processed using Origin® 6.0 and MatLab® 6.1 software.

Results and discussion

Results

The evolution with time of the (non-calibrated) Jet-REMPI concentration signal was registered simultaneously under 5 ionisation conditions[3] for compounds with molecular masses between 63 and 327 amu, focusing (Table 1) on non- to polychlorinated dibenzo-p-dioxins (DD), dibenzofurans (DF), benzofurans (BzF), pyrenes (Pyr), phenanthrenes (Phen), naphthalenes (N), and benzenes (Bz) and methyl substituted derivatives.

The main characteristics of the signal/time profile[3] observed are: (1) Baseline conditions before the reaction starts, (2) signal rising rapidly with temperature, (3) maximum of the signal, (4) its subsequent sharp and (5) slow further exponential decline until extinction. Signal physiognomy may be described by the moment (time, temperature) it first elevates above the baseline, the height, (+ time, temperature) when it reaches a maximum, the characteristics of the deep decline and the tail. The signal can also be integrated over the duration of the experiment, and the resulting surface forms a measure for the total

FORMATION AND SOURCES

evolved mass of the particular compound (Table 2 shows results for a standard experiment at 293 °C). Calibration factors established[3] for Bz, N, BzF, and DF allow deriving concentrations (ppm) and evolved amounts in µg (Table 3), both from 5 g of sample EU 12.

Products appear sequentially in time: at first, simple and polycyclic aromatics already during initial heating, and also mono-, di-, tri-, ... chlorinated compounds most *after* attaining setpoint. A later start delays reaching their maximum value and prolongs the tailing, partly cut off by the end of the run. DD shows much more tailing than DF. Also temperature affects product distribution. Benzene and naphthalene already appear at low temperature, whereas e.g. pyrene, methylpyrene, MCBz and MCDF are typically high temperature products, whereas DCBz is not, proving parallel formation!

Some signals are preceded by a low temperature peak, due to desorption of pre-existing aromatic compounds. Figure 1 shows the gradual transition in importance for Naphthalene from desorption dominated to reaction behaviour. Non chlorinated aromatics (Bz, Tol, N, BzF, Phen, Methylphen, DF, and DD) all show strong initial desorption, but the peak is poorly reproducible.

Discussion

The initial signal/temperature relationship, recorded during the heating of the sample, follows an Arrhenius relationship. Its activation energy is relatively low for aromatics, but quite high for some chlorinated compounds. Smoothening the signal retains the linear relationship, but affects activation energy values. The low activation energy for non-chlorinated aromatics indicates desorption as major phenomenon. Polychlorinated aromatics have high or even very high activation energies (Table 2, E_a) inferring that their signal is dominated by de novo formation.

Also the maximum signal height can be correlated using an Arrhenius type correlation, but the meaning of the resulting E-value is debatable, desorption shaping the low temperature peak of non-chlorinated aromatics and the 350 °C results being unreliable, since reaction run-away occurred and the signal attained saturation. Remarkably, monochlorinated aromatics always show the highest activation energy. Also the signal is highest for monochlorinated isomers, PCDD excepted. However, signals are non-calibrated, those in Table 3 excepted. Hence, there is a much higher sensitivity for aromatic structures than for (poly) chlorinated ones. The gradually declining final tail is well described by an exponentially decreasing curve, featuring a well-defined time constant of 0.7 to 2.3 $hour^{-1}$ at 293 °C, and 0.5 - 1 $hour^{-1}$ at 225 and 250 °C. The value of this time factor is remarkably constant and almost independent of chlorination level and temperature, ruling out a gradual desorption as a major factor determining the shape of the declining tail.

References

1. Hell K., Stieglitz L., Dinjus E., Segers P., Buekens A. Organohalogen Compounds: Formation and Sources-Posters, 2000, 46, 181-184
2. Hell K., Stieglitz L., Dinjus E., Segers P., Buekens A. Organohalogen Compounds: Formation and Sources-Posters, 2000, 46, 185-188
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Table 1. Mass of the homologues examined in this study, amu

Degree of chlorination	PCDD	PCDF	BzF	Naphthalene	Pyrene	Benzene	Phenanthrene
Non-C	184	168	118	128	202	78	178
MC	218	202	152	162	236	112	212
DC	252	236	186	196	270	146	246
TrC	286	270	220	230	304		280
TC	320	304	254	264			314
PeC				298			

Table 2. Results of monitoring at 258.9 nm. Experiment EU12-5 at 293 °C

Compound	Max signal[1], a.u.	Time of max signal[2], s	Surface under the curve [6], M a.u. · s	Start of signal increase		Duration of the process[3], min	Time factor[4], h[-1]	Ea[5], kcal/mol
				Time , s	Temper. , °C			
DD	246	1513	0.405	843	132	48 (10%)	1.184	3.6
MCDD	746	2116	1.723	1282	306	92 (10%)	1.566	*
DCDDs	590	2665	1.664	1884	321	>88 (e)	1.139	*
TrCDDs	255	4584	0.691	2651	308	>75 (e)	1.196	*
TCDDs	111	3651		Noise only			2.253	*
DF	2 420	1296	2.678	843	132	43 (10%)	1.887	6.8
MCDF	4 021	1349	5.455	1117	286	80 (10%)	1.689	103
DCDFs	1 465	1849	3.678	1337	310	>97 (e)	1.186	*
TrCDFs	640	3103	1.833	1610	321	>92 (e)	0.999	*
TCDFs	324	3377	0.900	2377	311	>80 (e)	1.109	*
Benzofuran	5 091	966	4.024	843	132	27 (10%)	1.799	8.5
MCBzF	3 081	1349	2.576	1062	273	37 (10%)	1.870	49.5
DCBzFs	395	1732	0.617	1610	321	59 (10%)	1.351	*
TrCBzFs	386	1896	1.113	1172	294	>100 (e)	0.870	*
TCBzFs	296	2884	0.959	1501	318	>94 (e)	0.704	*
Naphthalene	3 120	418	1.597	733	47	28 (10%)	1.376	8.5; 53
MCN	9 194	966	7.758	898	191	41 (10%)	2.197	93.8
DCN	4 632	1349	6.970	898	191	78 (10%)	1.562	9.5 ; 106
TrCN	513	1787	1.195	843	317	103 (10%)	0.811	*
TCN	120	5433	0.307	1665	322	>91 (e)	2.129	*
PeCN	67	4200		Noise only			0.772	*
Phenanthrene	10 616	582	7.454	898	191	34 (10%)	1.653	24.0
MCPhen	5 415	1842	10.28	1282	306	75 (10%)	2.063	110.2
DCPhen	2 288	2500	6.762	1665	322	>91 (e)	1.448	*
TrCPhen	249	4309	0.539	2816	307	>72 (e)	1.781	*
TCPhen	81	4419		Noise only				*
Benzene	32 199	582	23.38	733	47	24 (10%)	1.482	15.1
MCBz	1 049	1130	0.893	1337	310	37 (10%)		159.5

FORMATION AND SOURCES

DCBz	379	1185	0.674	843	132	67 (10%)	1.631	7.5; 41.8
Phenol	602	1157	1.138	843	132	94 (10%)		4.6; 172.5

1 – Within a series of homologues the sensitivity of Jet-REMPI declines strongly with rising degree of chlorination: e.g., equal signals observed for mono- and diCBz mean that the latter is more abundant.

2 – counted from the start of heating, s;

3 – period ranging from the initial increase of the signal till the moment it is reduced to 10 % of the maximum signal (marked "10 %") or till the end of the experiment (marked "e") if it is still higher;

4 – time factor θ from exponential decay fitting $y = A \bullet exp(-\theta \bullet x)$, where x=time and y=signal;

5 – values of activation energy are derived from the initial rapidly rising part of the non-smoothed curves; if two values of Ea are presented, it means that the first one corresponds to the first peak, and the second one to the second peak; * means no initial rise;

6 - integration was performed within the same time limits as stated above for the duration of reaction (see point 3) till reducing to either 10 % or the end of the test.

Table 3. Maximum concentration values (ppm) and total output (µg) recorded at various temperatures for Bz, N, BzF, and DF.

Temperature, °C	225	250	285	293	350
Concentration*, ppm					
Benzene, Bz	1.07	10.64	19.31	25.76	31.44
Naphthalene, N	1.10	2.00	2.86	2.96	36.86
Benzofuran, BzF	0.22	0.59	2.45	6.62	34.72
Dibenzofuran, DF	1.01	3.03	2.19	5.57	90.00
Amount**, µg					
Benzene, Bz	1.79	16.35	27.12	50.60	102.3
Naphthalene, N	1.29	3.01	6.89	6.53	147.8
Benzofuran, BzF	0.49	2.34	8.02	20.61	118.6
Dibenzofuran, DF	2.46	7.19	12.92	29.75	535.6

* gas flow rate=3 l/h;   ** on 5 g of sample, with a C-content of 3.8 %