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INVESTIGATION OF THE PYROLYTIC DEGRADATION OF ION EXCHANGE RESINS BY MEANS OF FOIL PULSE PYROLYSIS COUPLED WITH GAS CHROMATOGRAPHY / MASS SPECTROMETRY

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ABSTRACT

Cationic (LEWATIT S100) and anionic ion exchangers (LEWATIT M500MB) were thermally decomposed in amounts of 15 - 60 µg in a foil pulse pyrolyzer. The gaseous products were gas-chromatographically separated and identified by mass spectrometry. Cationic resins release mainly sulfur dioxide and benzene at temperatures up to 500°C. At higher temperatures, degradation products like ethylbenzene, styrene, hydrogen sulfide, benzene, and toluene are increasingly observed. Their ratio strongly depends on the applied temperatures. After fractionated pyrolysis of a single sample with rising temperatures, mainly benzene, hydrogen sulfide, and carbon disulfide are produced at 1000°C, leaving behind a residue of pyrolysis coke. Anionic resins generate mainly trimethylamine and methyl chloride up to 400°C. With rising temperatures, the formation of styrene, p-methylstyrene, and p-ethylstyrene dominates. Pyrolysis of anionic resins ends at about 900°C without leaving behind significant amounts of residue. Kinetic data for several of the observed degradation reactions were calculated.

INTRODUCTION

Cleanup of cooling water loops of nuclear power stations is accomplished with organic ion exchange resins. As a consequence of their radioactive contamination, these resins will not be regenerated and reused, but disposed of after a single application. Conventional disposal methods like cementation suffer from the risk of radiolytic or chemical degradation reactions occurring in the waste product, which may result in the destabilization of the waste container and in the emission of hazardous species into the environment. An alternate procedure could be combustion of the resins to chemically stable and much less toxic end products. This process is under development at the Jülich Research Center (1). It starts with a conditioning phase at temperatures of up to 800°C in an atmosphere with substoichiometric amounts of oxygen, resulting in pyrolytic decomposition reactions of the material. For process control purposes and in the case of failure conditions, it is important to know which pyrolysis products are being formed from different input materials with widely varying operating parameters.

Blasius gives a comprehensive survey of the characterization of 0.2-0.6 mg of synthetic ion exchange resins by pyrolysis - gas chromatography (PyGC) during 2 s at 770°C (2) and obtained fast fingerprint mass spectra from 0.35 mg of resin after 2 s of pyrolysis at 400 and 800°C (3). Parrish investigated single resin beads of 0.04-0.4 mg during a 10-s pyrolysis time by Curie point and filament pyrolysis at temperatures of 770, 800, and 980°C (4). Matsuda pyrolyzed 1 g of sulfonated cation exchange resin during 2 h at 200-800°C (5) and 200-600°C (6). Nassoy and Scanlan decomposed 12.5 g of sulfonated resin in an aqueous milieu during 24 h at 300°C, investigating the reaction products with PyGC - mass spectrometry (PyGC/MS) (7,8).

It seemed necessary to extend the investigations to a broader range of temperatures and reaction times, especially to combinations of rather short pyrolysis times and material amounts applying fractionated and sequential pyrolysis techniques, which avoid secondary chemical interactions and also permit the calculation of kinetic data.

EXPERIMENTAL METHODS

Materials

The ion exchange resins used in this study were of the types Lewatit M500MB (strongly basic, polystyrene with quaternary amine groups, chloride form, spherical particles 0.315-1.0 in mm diameter) and Lewatit S100 (strongly acid, polystyrene with sulfonic acid groups, sodium form, spherical particles 0.315-1.25 in mm diameter), both products of the Bayer Company, Leverkusen.

Instrumentation

The pyrolysis experiments were performed on a foil pulse pyrolyzer from the Pyrol AB, Sweden. The platinum foil (length 15 mm, width 2.6 mm, thickness 0.012 mm) was temperature calibrated with a photo diode in the range 570-1000°C. A resistivity measurement of the foil permitted the application of lower temperatures down to approximately 300°C. The initial current pulse duration was 8 ms and heated the foil to the desired temperature; the second pulse held the temperature during 200 or 2000 ms for conventional/sequential or fractionated pyrolysis. The pyrolysis chamber was held at 150°C with a carrier gas (He) flow of 13 mL min^{-1}. The chamber outlet was via a split (10:1) directly connected to a gas chromatograph (Siemens SiChromat 1). The pyrolysis gas passed an HT5 capillary column (Siloxane-Carborane copolymer, 25-m length, 0.32-mm ID, 0.1-µm film thickness, SGE Co., Australia), which was coupled to a mass spectrometer (ITD 800, Finnigan).

Procedures

Sample Preparation. The pyrolysis of single whole microspheres leads to an undesirable temperature gradient in the pyrogram, which is due to the relatively high heat capacity of the resin bead, compared to the platinum carrier foil. This can only be avoided with very small amounts of sample material. The material was dried for 17 h at 50°C / 70 mbar in a rotation evaporator, finely ground in a mortar mill, and suspended in chloroform/dichloroethane (2:1) for S100 and in dichloroethane for M500MB. A single drop of this suspension, carrying about 15, 30, or 60 µg of resin, was positioned into a small groove in the center of the platinum foil and the excessive solvent evaporated under an IR lamp. The aliquotation scatter was in the order of ± 10%. The obtained aliquot can be considered a representative fraction of the homogenous bead material.

Gas Chromatography / Mass Spectrometry. The injection port temperature was 200°C, temperature programs were 4 min/30°C - 10°C min^{-1}/30-280°C - 6 min/280°C (conventional pyrolysis), 4 min/30°C - 10°C min^{-1}/30-130°C (fractionated pyrolysis), and 60°C isotherm (fractionated and sequential pyrolysis). The carrier gas pressure was 80 kPa. The GC/MS transfer line was heated to 280°C. Peak identification and integration were performed using the ITD data system together with an NBS mass spectra library.

Conventional Pyrolysis. Single-sample aliquots are heated once for 200 ms to the desired temperature. Between consecutive experiments, the foil and the pyrolysis chamber have to be annealed in a bunsen flame. About 50 min are needed per experiment. This method delivers data for the identification of pyrolysis products at a certain temperature. An "afterpyrolysis" under such conditions of time and temperature, where the residual volatile components are totally released, may then permit the calculation of release rates for shorter pyrolysis time or at lower temperatures, presumed that no significant secondary reactions occur during the afterpyrolysis.

Fractionated Pyrolysis. A single sample is pyrolyzed consecutively in certain time intervals, e.g., 3 or 20 min (GC isothermal resp. temperature programmed), at rising temperatures, but for constant and relatively long periods of 2000 ms to attain equilibrium conditions at the given temperature level. From fractionated pyrolysis, information can be obtained about the formation characteristics of degradation products as a function of temperature and time. Fractionated pyrolysis is advantageous because multiple information is obtained in shorter time as compared to conventional pyrolysis.

Sequential Pyrolysis. A single sample is sequentially heated for short time periods (200 ms) until decomposition is complete. Pyrolysis temperature and time determine the necessary number of sequences. Data derived from sequential pyrolysis permit the calculation of kinetic parameters (9).

Data Evaluation. The peak areas of the total ion current (TIC) chromatograms were integrated using the ITD data evaluation system. A precise quantitation was not possible due to the unavoidable aliquot scatter and, in several cases, the unavailability of standards. Under certain conditions, the comparison of peak areas permits a reasonably good calculation of the formation yields of pyrolysis products, presumed the signal characteristics of the relevant components are not too different. For fractionated and sequential pyrolysis, the peak area of a single component was related to the total peak area of this component during all sequences; in conventional pyrolysis, the total of the first and the afterpyrolysis was used as the base for the calculation of single component yields.

RESULTS AND DISCUSSION

Conventional Pyrolysis of Anion Exchange Resin

Figure 1 shows a typical TIC pyrogram obtained with 15 µg M500MB after a 200-ms pyrolysis time at 700°C in helium atmosphere. Most of the peaks could be identified with the mass spectra library and by comparison with literature spectra (2, 3, 4, 10). The methylstyrene isomers, which have an almost identical fragmentation pattern, could only be distinguished after the acquisition of retention times and mass spectra of the pure substances. The dichloroethane

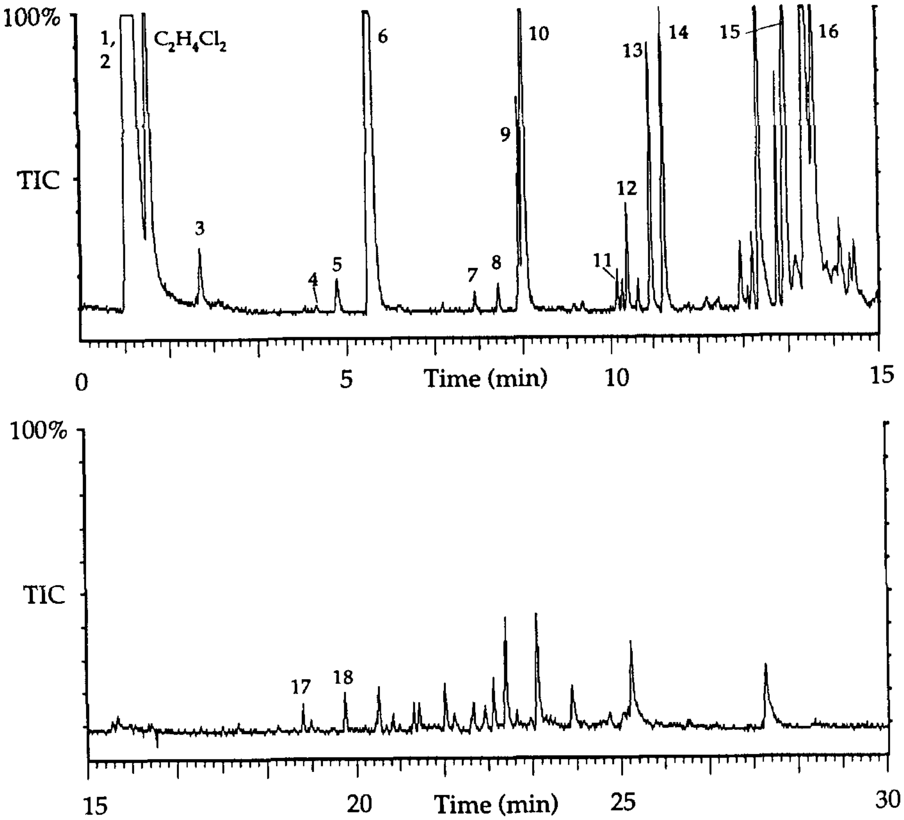

FIGURE 1. Total ion current pyrogram of 15 µg Lewatit M500MB at 700°C in helium atmosphere. The peak numbers correspond to the compounds listed in Table 1.

peak is due to residual solvent in the sample spot on the platinum foil. The identified components are listed in Table 1 in the order of elution.

To investigate the influence of sample size and pyrolysis temperature, about 15, 30, and 60 µg of M500MB were initially pyrolyzed for 200 ms at 570, 600, 700, 800, 900, and 1000°C and at the respective temperature afterpyrolyzed exhaustively. Methylchloride (MCL) and trimethylamine (TMA), for example, which are formed from the anchor groups, increase their formation ratio from

TABLE 1. IDENTIFIED PYROLYSIS PRODUCTS OF M500MB

Peak	Compound	m/z
1	Methylchoride	50
2	Trimethylamine	55
3	Toluene	91
4	Ethylbenzene	106
5	Xylene	106
6	Styrene	104
7	Ethyltoluene	120
8	α-Methylstyrene	117
9	m-Methylstyrene	117
10	p-Methylstyrene	117
11	m-Ethylvinylbenzene	132
12	p-Ethylvinylbenzene	132
13	m-Divinylbenzene	130
14	p-Divinylbenzene	130
15	Isoquinoline	129
16	Dimethylindole	144
17	1,3-Diphenylpropane	196
18	2,4-Diphenyl-1-butene (Styrene dimer)	208

TABLE 2. INFLUENCE OF TEMPERATURE AND SAMPLE SIZE ON THE M500MB PYROLYSIS YIELDS OF METHYL CHLORIDE (MCL) AND TRIMETHYLAMINE (TMA)

T	Sample	Area * 10^3		Ratio
(°C)	(μg)	MCL	TMA	MCL/TMA
570	15	61.8	69.8	0.89
	60	94.7	283.9	0.33
600	15	63.8	71.3	0.89
	30	221.9	275.2	0.81
	60	111.8	314.2	0.36
700	15	65.2	81.9	0.80
800	15	59.2	67.8	0.87
900	15	55.9	51.9	1.08
1000	15	66.6	46.1	1.44

0.9 to 1.4 with increasing temperature (see Table 2), resulting from an absolute decrease of the TMA formation, whereas their formation ratio decreases with increasing sample size from 0.9 to 0.3 in the temperature range 570-600°C. Other components show a temperature dependent shift of their area fractions compared to the total area of all significant degradation products with increasing temperature (Figure 2): the area fraction of TMA decreases from 23 to 11% in the range of 700-1000°C, whereas the area fraction of p-ethylvinylbenzene increases from 0.8 to 9%, and other main components like MCL, styrene, and p-methylstyrene keep their area fractions almost constant. It was generally observed that the samples were degraded to 98-100% already during the initial 200-ms pyrolysis period.

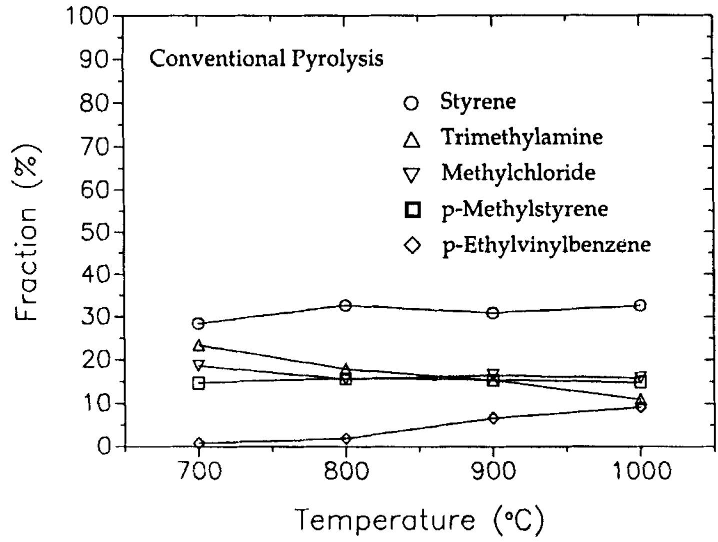

FIGURE 2. Formation of conventional pyrolysis products from M500MB as a function of temperature.

Fractionated Pyrolysis of Anion Exchange Resin

About 30 µg of M500MB were pyrolyzed consecutively in time intervals of 3 min for 2000 ms each at 300, 400, 500, 550, 600, 700, 800, 900, and 1000°C. Figure 3 shows two groups of decomposition products. TMA and MCL, originating from the anchor groups, reach their formation maximum already at temperatures below 300°C, whereas other main components resulting from the decomposition of the resin matrix material (e.g. styrene, p-methylstyrene and p-ethylstyrene), have their maximum formation between 550 and 600°C.

These results permit the definition of the working temperature in sequential pyrolysis. According to Figure 3, a temperature of between 500 and 550°C and a reasonably short pyrolysis time allow a sufficient number of steps to generate a data base for kinetic studies.

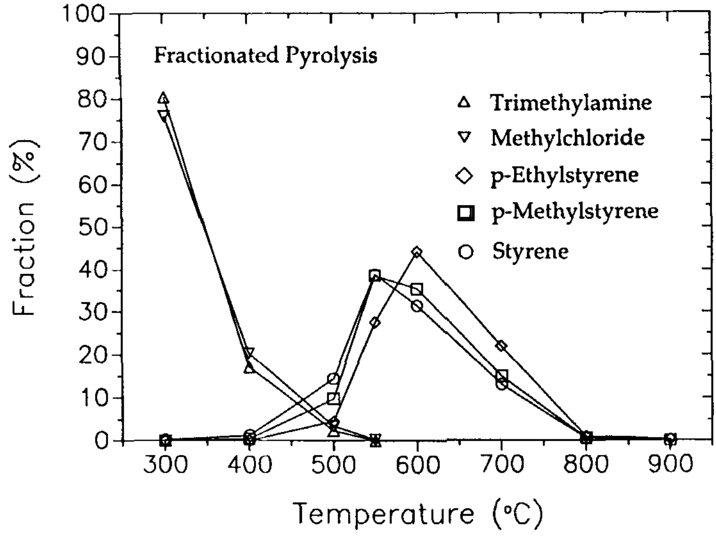

FIGURE 3. Formation of fractionated pyrolysis products from M500MB as a function of temperature.

Sequential Pyrolysis of Anion Exchange Resin

About 15 µg of M500MB were pyrolyzed sequentially in time intervals of 3 min for 200 ms each at 570, 600 and 630°C. Figure 4 shows the formation of styrene and p-methylstyrene as a function of pyrolysis time and temperature. It is evident that already at 570°C and after 200 ms these compounds have reached about 50% of the total yield and that at 630°C and after 1 s their yield approaches 100%. The obtained data were used for kinetic calculations.

Conventional Pyrolysis of Cation Exchange Resin

Figure 5 shows a typical TIC pyrogram obtained with 60 µg S100 after a 200-ms pyrolysis time at 800°C in a helium atmosphere. It is in good agreement with that of Blasius (2), who, under quite different conditions, pyrolyzed 0.2-0.6 mg of a Dowex 50 WX12 resin for 2 s at 770°C in a steel capillary. The products

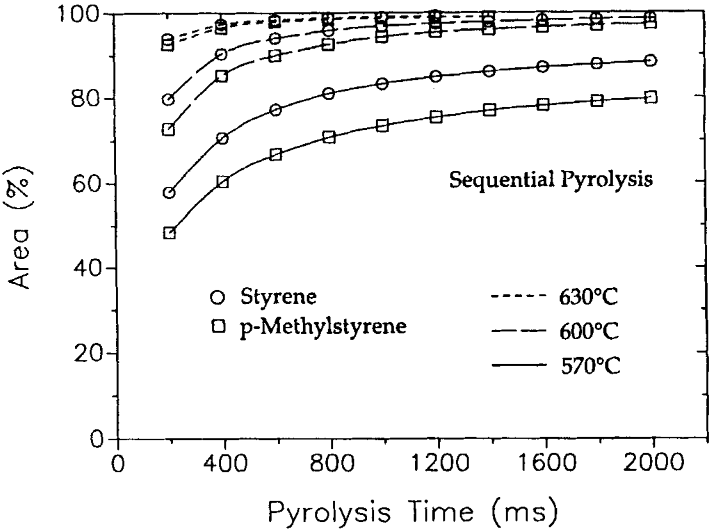

FIGURE 4. Formation of sequential pyrolysis products from M500MB as a function of pyrolysis time.

of the actual experiment were identified as described before and are listed in Table 3.

Samples were pyrolyzed at 570, 600, 700, 800, 900, and 1000°C, followed by an afterpyrolysis at 1000°C. Figure 6 shows the relative yields of the main decomposition products as a function of temperature.

The styrene fraction increases significantly from 4 to 21%, whereas SO_2 decreases slowly from 66 to 58%, CS_2 and H_2S appear above 900°C reaching 2 to 4% at 1000°C, and benzene and ethylbenzene keep almost constant at the 2% level.

Although twice the amount of resin was used compared to the pyrolysis of M500MB, the peak area total was considerably smaller than before. It is explained by the observation that after pyrolysis of the acid resin a black residue remains on the foil, whereas the basic resin is almost totally decomposed at

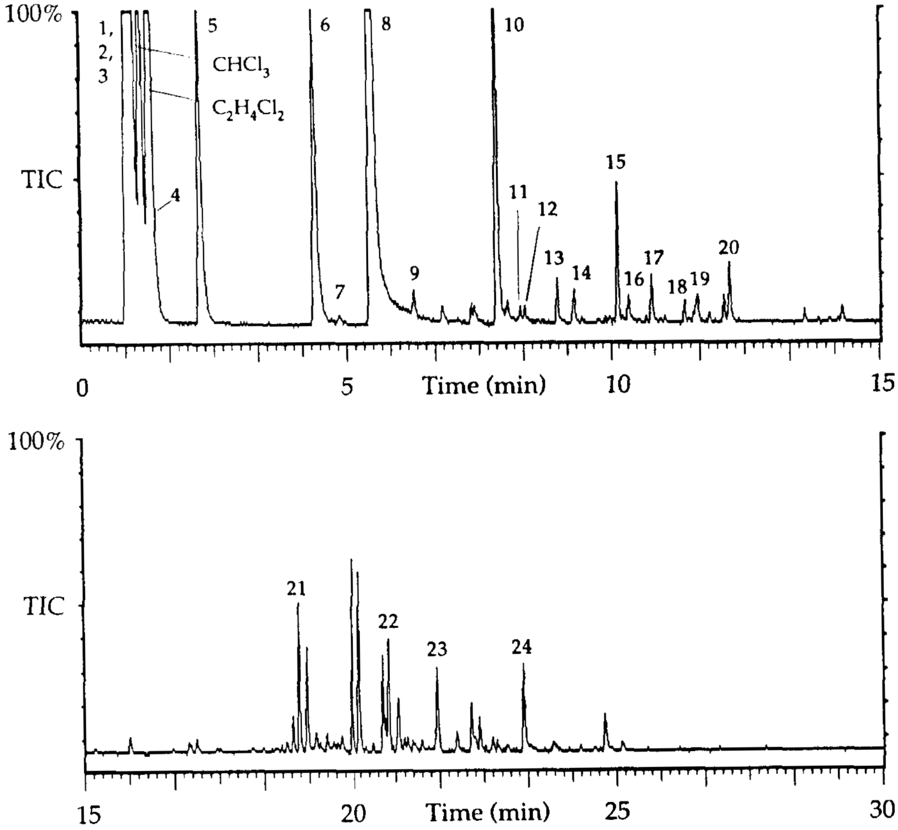

FIGURE 5. Total ion current pyrogram of 60 µg Lewatit S 100 at 800°C in helium atmosphere. The peak numbers correspond to the compounds listed in Table 3.

relatively low temperature. This is in agreement with Matsuda (6), who found a 50% decomposition at 600°C for an acid resin and a 90% weight loss of basic material already at 400°C.

Fractionated Pyrolysis of Cation Exchange Resin

About 60 µg of S100 were treated under the same conditions as M500MB. Figure 7 shows two maxima for benzene at 500 and 800°C and a plateau for

TABLE 3. IDENTIFIED PYROLYSIS PRODUCTS OF LEWATIT S100

Peak	Compound	m/z
1	Hydrogen sulfide	34
2	Sulfur dioxide	64
3	Carbon disulfide	76
4	Benzene	78
5	Toluene	91
6	Ethylbenzene	106
7	Xylene	106
8	Styrene	104
9	Cumene	120
10	α-Methylstyrene	117
11	m-Methylstyrene	117
12	p-Methylstyrene	117
13	Indan	117
14	Indene	115
15	m-Ethylvinylbenzene	132
16	p-Ethylvinylbenzene	132
17	m-Divinylbenzene	130
18	p-Divinylbenzene	130
19	Naphthalene	128
20	Benzothiophene	134
21	1,3-Diphenylpropane	196
22	1,2-Dihydro-4-phenylnaphthalene	206
23	Phenylnaphthalene	204
24	Phenylmethylnaphthalene	218

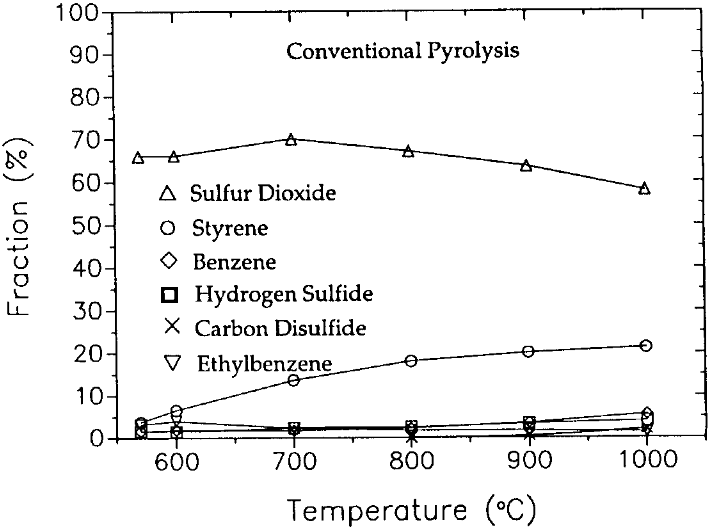

FIGURE 6. Formation of conventional pyrolysis products from S 100 as a function of temperature.

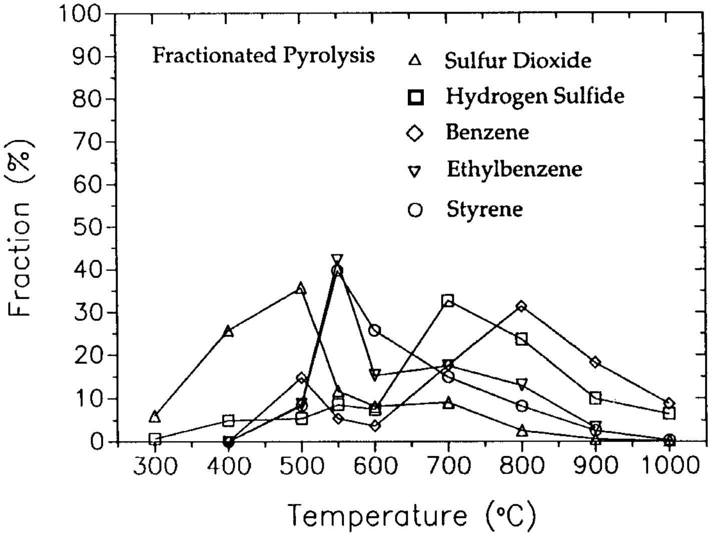

FIGURE 7. Formation of fractionated pyrolysis products from S 100 as a function of temperature.

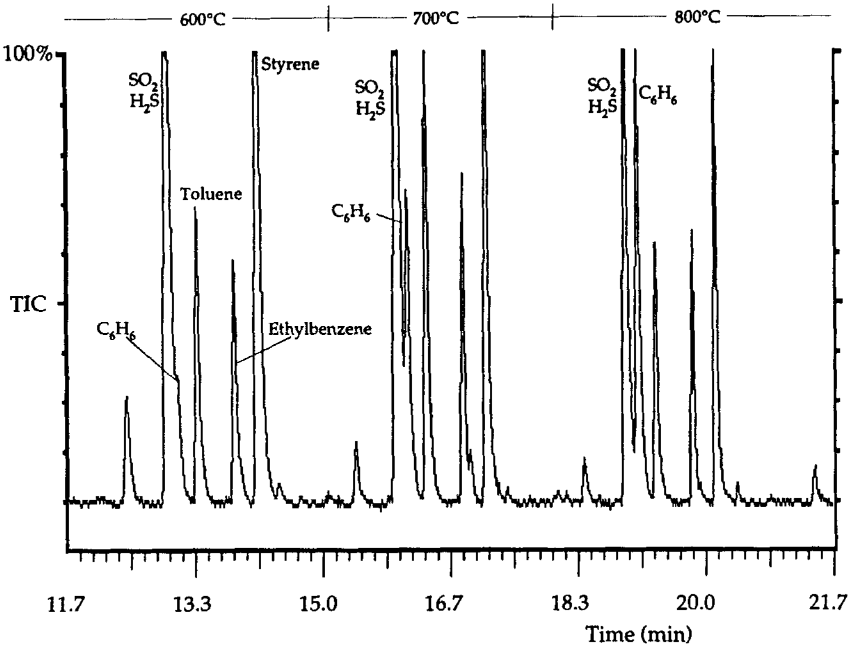

FIGURE 8. Temperature-dependent resolution of SO_2 and C_6H_6 peaks in fractionated pyrolysis of S 100.

ethylbenzene and SO_2 between 600 and 700°C. An explanation could be the formation of sulfonyl- and sulfur groups at 300-400°C in the polymer structure, as described by Matsuda (5, 6), stabilizing the structure thermally up to about 600°C, followed by bond breaking at > 700°C, again formation of the mentioned compounds and increasing amounts of H_2S and CS_2. Blasius (2) supposed the formation of H_2S during pyrolysis of acid resins; Nassoy and Scanlan (7) also found CS_2 in their investigations. The significant increase of the styrene yield from 14 to 24% in the temperature range 700-1000°C in conventional pyrolysis (Figure 6) also indicates a continued cracking of the polymer structure.

Fractionated pyrolysis offers a chromatographic separation effect, which can assist the identification of decomposition products. Figure 8 shows benzene

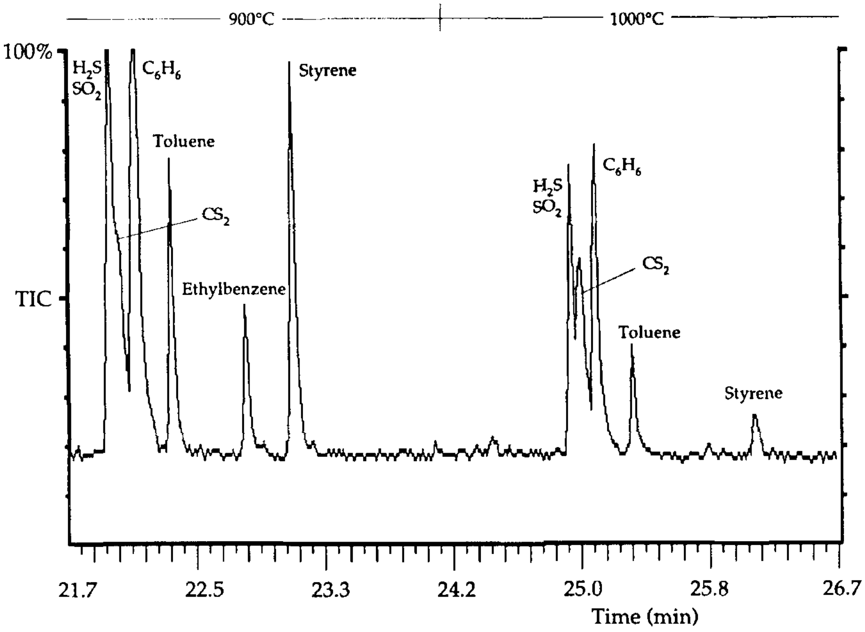

FIGURE 9. Temperature-dependent resolution of H_2S and CS_2 peaks in fractionated pyrolysis of S 100.

as a trace shoulder on the SO_2/H_2S peak at 600°C; the separation is partial at 700°C and nearly complete at 800°C. Analogously, CS_2 separates from H_2S/SO_2 at a 1000°C pyrolysis temperature (Figure 9), appearing as a shoulder only at 900°C.

Sequential Pyrolysis of Cation Exchange Resin

S100 samples were pyrolyzed as described for M500MB, but with 40-60 µg instead of 15 µg to compensate for the lower yield of volatiles from acid resin. Figure 10 shows the formation of styrene and ethylbenzene as a function of pyrolysis time and temperature. It demonstrates again a somewhat higher thermal stability of acid resin at relatively low temperature (570°C) compared to

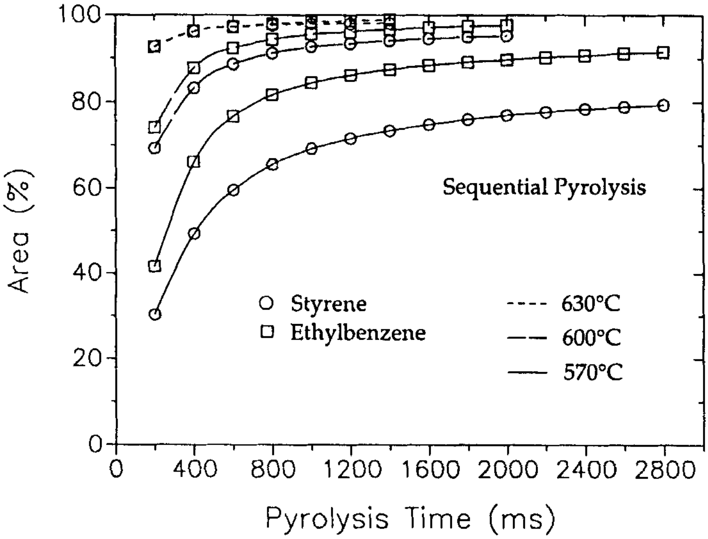

FIGURE 10. Formation of sequential pyrolysis products from S 100 as a function of pyrolysis time.

M500MB. The difference becomes marginal at temperatures > 600°C. Also these data were used for kinetic calculations.

Kinetic Calculations

Sequential pyrolysis of a styrene polymer results in the same amount of degradation products as conventional pyrolysis after an equivalent pyrolysis time (11). This permits a rapid generation of raw data for kinetic calculations, which otherwise could only be obtained after a respective number of conventional pyrolysis runs. Assuming a first-order reaction according to Equation (1), the rate constant, k, for different pyrolysis temperatures is represented by the slope of Equation (2).

$$\text{Polymer} \rightarrow \text{A} + \text{B} + \ldots \qquad (1)$$

$$-\ln\left(1-\sum_{1}^{n} A_{x,n} \Big/ \sum_{1}^{n=m} A_{x,n}\right)=k\cdot t \qquad (2)$$

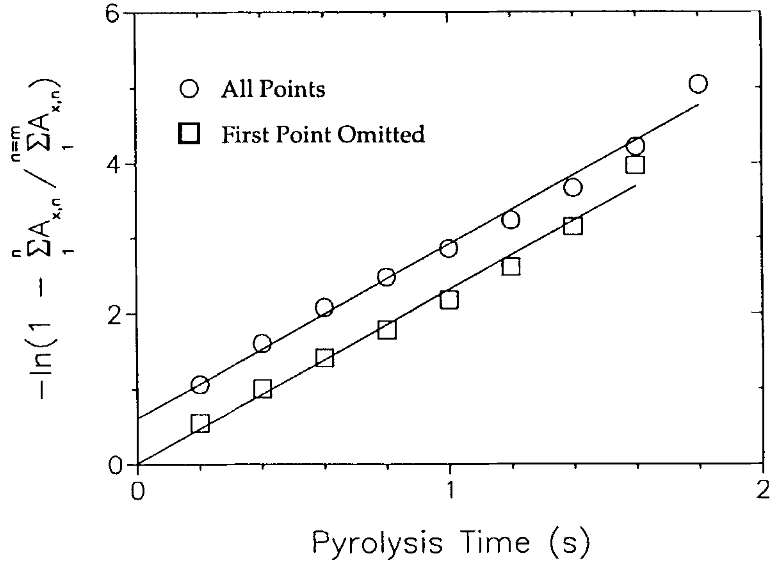

FIGURE 11. Kinetics of the styrene formation from 15 μg M500MB during sequential pyrolysis at 570°C.

In Equation (2), A_x is the peak area of product x of the sequential pyrolysis number n in series, m is the number of the last sequential pyrolysis in series of the same run, and t is the reaction time in s. The points of the top curve of Figure 11, calculated with Equation (2), result from the formation of styrene during the sequential pyrolysis of 15 μg M500MB. It is remarkable that the points, to which a linear regression line is approximated, show a slightly S-shaped characteristic, and that the function does not, as should be expected, pass through the coordinate origin.

The first observation is explained by the fact that Equation (2) is strictly valid only if $m = \infty$. This cannot be achieved practically; a limited value of m induces the observed shape just for mathematical reasons.

The mismatch with the coordinate origin results from a continuous change of the k values in the course of pyrolysis progress, caused by a fast degradation

TABLE 4. RATE CONSTANTS, k, AND ACTIVATION ENERGIES, E, CALCULATED FROM SEQUENTIAL PYROLYSIS

T (°C)	k (s^{-1})			
	S100		M500MB	
	Styrene	Ethyl-benzene	Styrene	p-Methyl-styrene
570	1.7	1.7	2.3	2.2
600	2.4	2.3	3.1	3.2
630	3.5	2.9	4.1	4.3
E (kJ· mol^{-1})	64	48	47	53

reaction in the beginning, which slows down with time, leading, however, always to the same pyrolysis product. This can be explained by the change of polymer structure during pyrolysis. Under pyrolytic conditions, polymers, especially of the styrene-divinylbenzene cross-linked copolymer-type resin under investigation, carbonize progressively under release of low-molecular-weight hydrocarbons. This leads to a thermal stabilization, decreasing the speed of the pyrolysis reaction. The effect is predominant in the initial pyrolysis steps, so that by omitting only the first 200-ms measurement value from the evaluation, the resulting lower function in Figure 11 now almost passes through the origin. The k values given in Table 4 therefore approximate the pyrolysis conditions after a relatively long reaction time for the main products styrene and p-methylstyrene from M500MB, and styrene and ethylbenzene from S100, as well as the activation energies, which were calculated from the slopes of the Arrhenius plots.

CONCLUSIONS

The pyrolytic degradation of ion exchange resins leads to a large number of products which can only partially be identified. The product pattern is, however, typical for different resin types and allows a fingerprint identification with only very small amounts of sample material, which is important for an unambiguous identification and also if radioactive loaded resins have to be checked.

The identified degradation products are in the range of an intermediate level of toxicity. The search for ultratoxic compounds like dioxins and furanes, the formation of which cannot totally be excluded, was, for technical reasons, not possible within the scope of these experiments.

Foil pulse pyrolysis is a valuable tool for the investigation of degradation reactions under controlled conditions of temperature, reaction time, and atmosphere and again with sample amounts in the µg range. This is a prerequisite for the calculation of kinetic parameters.

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