Communication

Chemical Reactions in Supercritical Water – 1. Pyrolysis of tert.-Butylbenzene*)

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Supercritical water is a powerful solvent and a favourable reaction medium for oxidation of organic material. The role of supercritical water in these processes is not fully understood. The influence of supercritical water on the pyrolysis of tert.-butylbenzene as a model compound was investigated. Experiments were carried out in a flow reactor at pressures between 5 and 25 MPa, at temperatures between 505 and 540 °C and residence times between 15 and 55 s. Water, nitrogen, and water-nitrogen mixtures, respectively, were used as reaction media; no significant differences in the product formation rates and distributions were detected. In an experiment with D_2O, instead of H_2O, it was proved, that deuterium is incorporated in all the product substances in various amounts. Interpretating the results with a reaction model based on a radical mechanism it was made probable that H-D exchange reactions occur with radical intermediates.

Introduction

Supercritical water SCW ($T > 374\,°C$, $p > 22.1$ MPa) shows extraordinary physical and chemical properties [1]. The density can be varied continuously from gas like to liquid like values. Viscosity decreases significantly, and the solubility of organic compounds increases. The dielectric number varies continuously in a wide range depending on temperature and pressure. As the viscosity is low [2] and therefore the diffusion high, space-time yields of chemical reactions in SCW are often large. Therefore the supercritical state is favourable for chemical reactions, for which higher conversions are required.

Recently, kinetic studies on hydrolysis and pyrolysis of various polar organic compounds in SCW and hydrothermal oxidations of small organic molecules were reported [3–9]. Investigations of the pyrolysis of non-polar compounds in supercritical water are rather scarce [10, 11]. The question whether water is directly involved in the mechanism of reactions in SCW has been disregarded so far.

In this work an answer to this question is attempted by an experimental comparison between pyrolysis reactions in SCW, nitrogen, and nitrogen-water mixture and investigations in supercritical heavy water (SCDW). Tert.-butylbenzene (TBB) was employed as a model compound for the pyrolysis to choose a relative simple substance containing an aromatic and an aliphatic structure.

Experimental

The apparatus, described in detail elsewhere [12, 13], consists of the feeding device, preheaters, the flow reactor, a cooler, an expansion valve, and a sampling device. The pressure in the reactor could be varied from 5 to 25 MPa and the temperature from 505 to 540 °C. Prior to feeding to the apparatus, the process water was saturated with argon to replace dissolved oxygen from air. Nitrogen and TBB were used without any pretreatment. The three flows were metered separately and then fed to mixing chambers, which are specially devised for fast and efficient mixing. The reactor consists of a 6 m long stainless steel tube (2 mm i.d.) immersed in a fluidized sand bath to ensure isothermal reaction conditions. The temperature at both ends and along the tube was controlled by 6 Ni-NiCr thermocouples. The effluent leaving the reactor was quenched in a heat exchanger down to a temperature of 17 °C and its pressure was reduced to atmospheric by a back pressure regulating valve. The liquid and vapour phases were metered and separately collected. The composition of the gas phases was analysed by gas chromatography. Liquid phases were extracted by n-pentane to separate TBB and products from water and then also analysed by gas chromatography. Most of the product compounds were identified either by mass spectrometry or by gaschromatographic comparison with known compounds.

In a series of experimental runs (total number 50) the overall pressures, temperatures and feed flow rates – and therefore also the residence times – were varied in certain limits. In Table 1 these data are listed for experiments in the 5 different reaction media (water, nitrogen, two different water-nitrogen mixtures, and heavy water) together with the variations of these conditions.

Results and Discussion

From the composition of the gaseous and liquid phases of the product streams, conversions were calculated. The concentration of TBB (Fig. 1) and the formation of the main

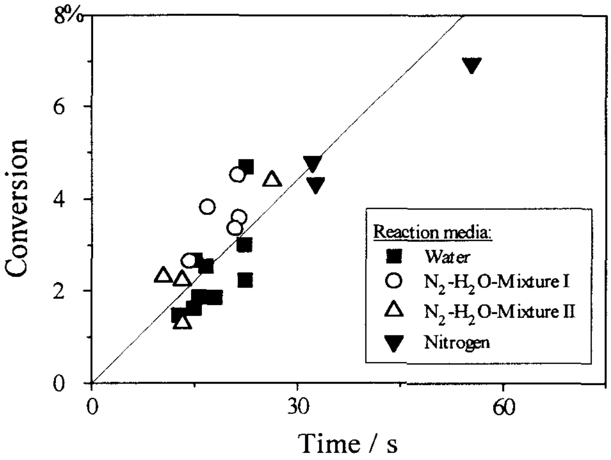

Fig. 1
Conversion of TBB as a function of reaction time in supercritical water, nitrogen, and nitrogen-water mixtures at 25 MPa and 535 °C

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Table 1
Reaction conditions [13] of experimental runs

Number of experiments	Reaction media	Pressure (MPa)	Temperature (°C)	Nitrogen flow (g/h)	Water flow (g/h)	Tert.-Butylbenzene flow (g/h)
28	Water	5 – 25	500 – 540	–	600 – 1200	30 – 60
7	Mixture I	25	500 – 540	28 – 40	600 – 900	30 – 60
7	Mixture II	25	500 – 540	320 – 640	600 – 700	30 – 60
7	Nitrogen	25	500 – 540	320 – 640	–	30 – 60
1	D_2O	25	535	–	600	30

products benzene, toluene, iso-butylbenzene, cumene, and α-methylstyrene are considered. A more detailed description of the analytical results of all product substances is given elsewhere [13]. Due to the constraints of the experimental conditions (flow rates of the pumps, maximum temperature of the sandbath, reactor length etc.) conversions were limited to app. 7%.

Fig. 2 shows a typical gas chromatogram of a liquid product phase. Such diagrams were used to evaluate the respective kinetic data for the formation of products. All of the peaks containing more than 0.1‰ of the product mixture have been identified. The gas phase was much less in variety and contained predominantly hydrogen, methane, ethane, ethene, propane, propene, iso-butane, and iso-butene. In Fig. 3 the formation-time diagrams for the two main products cumene and α-methylstyrene are shown. In both cases no significant differences in the product formation and the kinetics were observed between reactions in supercritical water, pure nitrogen, and nitrogen-water mixtures. An inspection of the formation data of other products shows an analogous behaviour. The variety and distribution of the product species indicate that the reaction proceeds by a free radical mechanism.

It had to be proved whether participation of water in the reaction would lead to the formation of hydroxyl-compounds. Careful analysis of the product mixtures gave no evidence for such substances in the reaction mixture, even in minor quantities. Therefore such reactions can be definitely excluded. Hydrogen exchange is another possibility for an impact of the water environment to the reaction. This can readily be proven by the application of heavy water instead of light water. It was confirmed that a catalytic H-D exchange did not occur under the conditions applied, because tert.-butylbenzene in the product mixture did not show any H-D exchange. However, all of the product substances investigated show substantial deuterium contents in varying quantities, as detected by mass spectrometry. This proves that water plays a role within the radical chain mechanism.

Analysis of different products shows different H-D exchange rates. The results of 5 main products are listed in Table 2. It is assumed that only one H-atom is replaced by D per molecule.

To discuss these phenomena, the reaction model, which has been developed for the TBB-Pyrolysis [13], was reduced to the formation of the 5 main products (Fig. 4). Radical in-

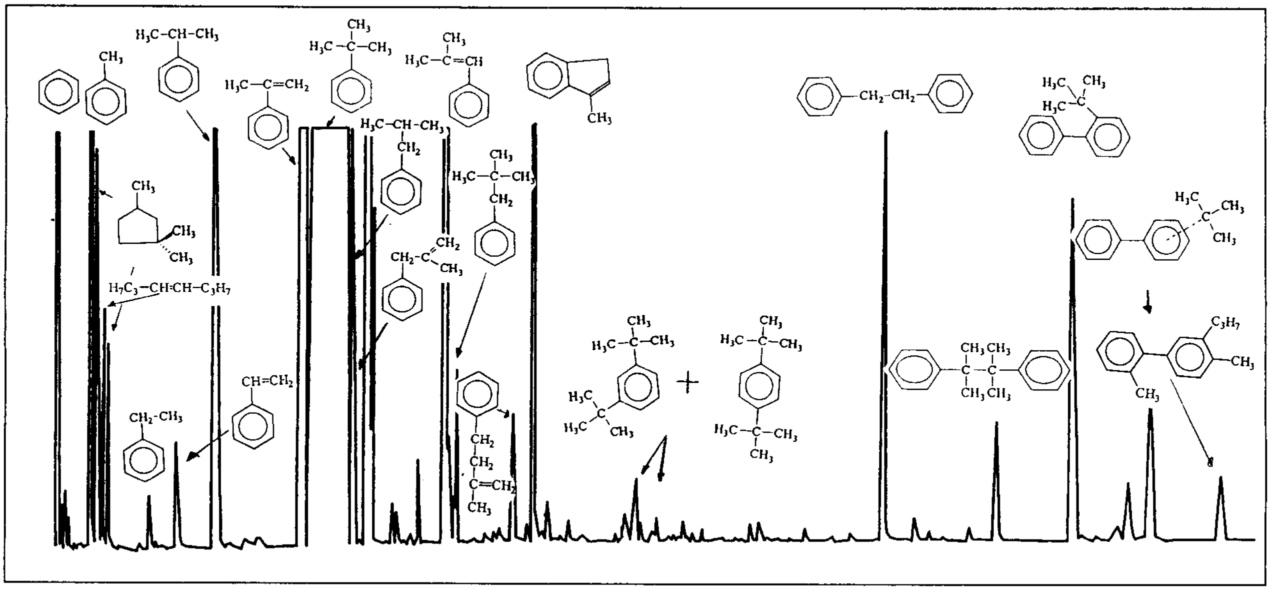

Fig. 2
Chromatogram of liquid products after the reaction of TBB in supercritical water at 25 MPa and 540 °C (Conversion 4%)

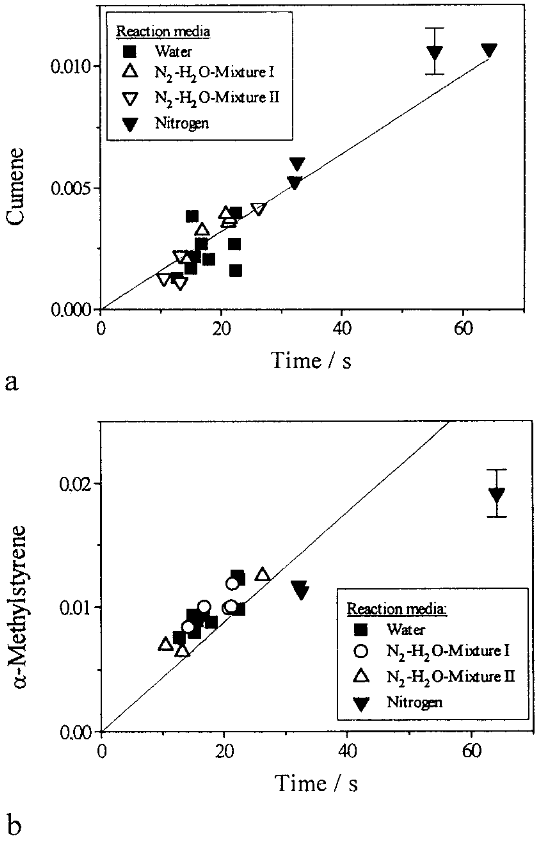

Fig. 3
Formation of cumene (a) and α-methylstyrene (b) as a function of reaction time in supercritical water, nitrogen, and nitrogen-water mixtures at 25 MPa and 535 °C (Ordinate: Molar fraction in the product mixture including TBB and reaction products.)

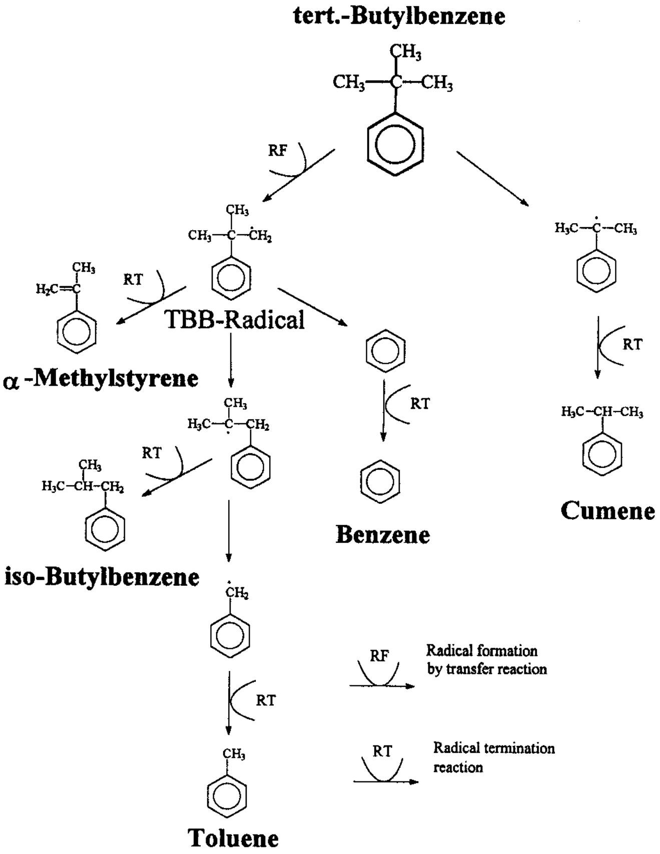

Fig. 4
Simplified mechanism for the formation of α-methylstyrene, iso-butylbenzene, toluene, benzene, and cumene (not stoichiometric)

itiation of TBB by cleavage of one aliphatic C-C bond leads directly to cumene. Only one radical species is involved in this reaction. Radical formation by transfer results in the TBB-radical, which disintegrates in three different reaction paths. The elimination of iso-propene leads to the phenyl radical and finally to benzene. As the phenyl radical is very reactive, a high H-D exchange rate is expected. The elimination reaction of the TBB-radical yields in α-methylstyrene, which should contain less deuterium because of the abstraction of a methyl radical. The TBB-radical undergoes rapid isomerization and the resulting new radical (1-phenyl-2-methyl-2-propyl radical) reacts either to iso-butylbenzene or disintegrates to form the relatively stable benzyl radical. As iso-butylbenzene has not lost any hydrogen a relatively high exchange rate is expected, compared to that of α-methylstyrene. As the lifetime of the benzyl radical is high, the probability of an H-D exchange should be enhanced. Following the above argumentation the measured H-D exchange rate ranking from 23% for benzene to 11% for α-methylstyrene becomes reasonable. Work to model these reactions in the context of a more detailed mechanism is in progress and will be reported elsewhere. The present results show that H-D exchange rates depend on the life time of the radical and the number of the radicals within the reaction pathways.

Table 2
Percentage of mono-deuterated molecules of some selected products

Product	Mean molar fractions of liquid products in %	Percent of mono-deuterated molecules (±2)
Benzene	26	23
Toluene	8	19
iso-Butylbenzene	18	17
Cumene	8	14
α-Methylstyrene	31	11

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