



## Research article

Quantification of reactive intermediate radicals and their induction effect during pyrolysis of two *n*-alkylbenzenesZezhou Chen<sup>a</sup>, Xurui Zhang<sup>a</sup>, Zhenyu Liu<sup>b,\*</sup>, Qingya Liu<sup>a,\*</sup>, Teng Xu<sup>c</sup><sup>a</sup> State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China<sup>b</sup> Beijing Advanced Innovation Centre for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China<sup>c</sup> ExxonMobil Chemical Company, Baytown, TX 77520, USA

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## ABSTRACT

Pyrolysis of heavy organic resources follows the radical mechanism. It involves the reactions between radicals generated from the cleavage of covalent bonds in a reactant and the reactions between the radicals and the reactant. The radicals are the reactive intermediates that govern the rate and product distribution of pyrolysis. This paper quantifies the reactive intermediate radicals generated in direct pyrolysis of two *n*-alkylbenzenes and the induced pyrolysis of the alkylbenzenes by the radicals, based on the data obtained in pyrolysis with and without tetralin that is able to donate hydrogen radicals. It is found that about 90% reactive intermediate radicals can be capped by the hydrogen radicals from tetralin. At 400–440 °C the contribution of induced pyrolysis is more than that of direct pyrolysis, about 1.9 times for *n*-propylbenzene and 3 times for *n*-pentylbenzene. The role of induced pyrolysis is larger at higher temperatures due to its higher activation energy than direct pyrolysis.

## 1. Introduction

Pyrolysis is a major technique to convert solid organic resources and wastes, such as biomass, heavy petroleum, coal, and waste tire and plastics, to clean and value-added fuels and chemicals. Pyrolysis is well recognized to follow the radical mechanism, which generally involves two steps: the cleavage of covalent bonds to generate free radical fragments and the reactions of the radical fragments [1,2]. The pyrolysis usually starts in the temperature range of 350–400 °C due to the cleavage of weak covalent bonds such as C<sub>al</sub>–O, C<sub>al</sub>–S and C<sub>al</sub>–C<sub>al</sub>, and complete at temperatures around 600 °C to maximize the volatiles generated [3]. These reactions of radical fragments include coupling, disproportionation and condensation, while the condensation also generates radicals. The reactions of radical fragments also include the reaction of radicals with the reactant [1,4,5], in which the radicals induce the reactant to be pyrolyzed at a lower temperature and a higher rate [6,7], or promote aromatization of the reactant [8,9]. Clearly, the radical fragments are the reactive intermediates that govern the rate and product distribution of pyrolysis.

The reactions of radical fragments (termed radicals in short thereafter) has been studied in pyrolysis of complex organic resources such as biomass [10], coal [11], oil shale [12] and heavy oil [13], as well as in pyrolysis of simple hydrocarbons such as alkylbenzene [14]. It was

found that the generation of primary radicals from the reactant depends on their bonding structure [15–18] especially the alkyl C–C bond in β-position from the aromatic ring [14], while the abstraction of H from the reactant by the radicals occurs mainly on aliphatic chains, preferably at the α-position from aromatic rings, which induces the reactant to crack [14,19].

The induction effect of radicals on pyrolysis of ethyl-, *n*-propyl-, and *n*-butyl-benzene has been studied qualitatively using toluene [20] and aniline [21] as hydrogen radical (H·) donors. These solvents, however, yield benzyl and aniline radicals, respectively, after providing H·, which participate in the reaction and make the quantification of H· and the reactive intermediate radicals from the reactant difficult. Since tetralin forms naphthalene and dihydronaphthalene after providing H· and these compounds are stable and do not couple with the reactant, it should be a better H· donor solvent to quench and quantify the reactive intermediate radicals in pyrolysis. This approach, however, has not been reported in the literature.

This work quantifies the primary radicals generated in pyrolysis of *n*-propylbenzene (*n*-PrB) and *n*-pentylbenzene (*n*-PeB) and the radical induced pyrolysis in a temperature range of 400–440 °C. The rationale of the study is shown in Fig. 1 that includes two pyrolysis routes, direct pyrolysis (DP) of the alkylbenzenes to generate primary radicals and induced pyrolysis (IP) of the alkylbenzenes by the primary radicals. The

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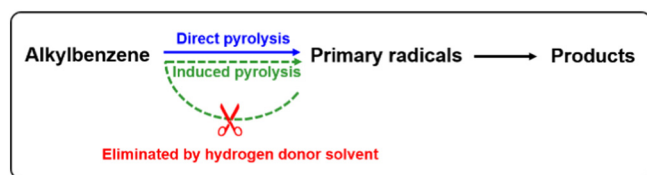


Fig. 1. Reaction scheme of alkylbenzene pyrolysis and the role of hydrogen donor solvents.

former is determined by capping the primary radicals with  $\text{H}\cdot$  donated from tetralin which eliminates the route of IP as well as other reactions between the primary radicals. The latter is determined as the difference between pyrolysis without and with tetralin. In principle, this work simulates the reactions in pyrolysis of many organic resources, although they are more complex in structure and in reaction pathway than the alkylbenzenes.

## 2. Experimental

### 2.1. Thermal reaction of the *n*-alkylbenzenes

The *n*-alkylbenzenes used were analytical grade *n*-PrB and *n*-PeB. The tetralin was greater than 99.9% in purity. Each experiment used  $64\ \mu\text{mol}$  alkylbenzene (around  $10\ \mu\text{l}$ ) with or without  $256\ \mu\text{mol}$  tetralin. The pyrolysis was carried out in glass tubes of 2 mm in diameter and 40 mm in length with a volume of 0.125 ml. The glass tubes were purged with  $\text{N}_2$  for 15 s before being fuse-sealed by a burner. The sealed glass tubes were then inserted into slots of a pre-heated heater for 5, 10, 20 and 30 min. Preliminary experiments showed that the *n*-alkylbenzenes in the glass tubes were heated to the desired temperatures in less than 2.5 min without overshooting. After the glass tubes were cooled to room temperature, each of them was put into a latex tube that was purged with Ar and then sealed. The glass tube in the latex tube was broken to allow the gaseous products to diffuse into the latex tube.

The gas in the latex tube was sampled by a syringe and analyzed by a gas chromatography (GC-2018, Shimadzu) with a FID detector and an  $\text{Al}_2\text{O}_3$  column. The oven temperature was  $60\ ^\circ\text{C}$  for 3 min,  $60\text{--}150\ ^\circ\text{C}$  at a rate of  $10\ ^\circ\text{C}/\text{min}$ , and  $150\ ^\circ\text{C}$  for 10 min. The liquid remained in the glass tube was diluted with 0.5 ml hexane and then analyzed by a gas chromatography (7820A, Agilent) with a FID detector and a HP-5 column. The temperature was  $80\ ^\circ\text{C}$  for 15 min,  $80\text{--}240\ ^\circ\text{C}$  at a rate of  $10\ ^\circ\text{C}/\text{min}$ , and  $240\ ^\circ\text{C}$  for 10 min. The procedure is schematically shown in Fig. 2. The GC areas of *n*-PrB, *n*-PeB, tetralin, naphthalene, dihydronaphthalene and other compounds formed were quantified by external calibration using corresponding pure compounds.

At least two repeat experiments were made at each condition and

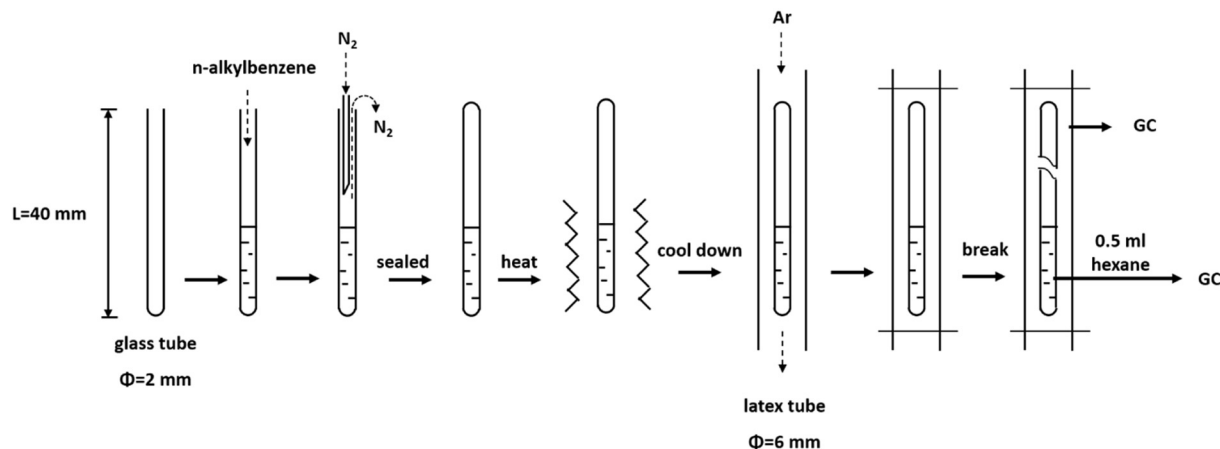


Fig. 2. The experimental procedure.

the overall experimental errors are less than 4%. The detection limits in quantification of the products are  $0.02\ \mu\text{mol}$ .

### 2.2. Quantification of $\text{H}\cdot$ donated from tetralin

As discussed earlier, tetralin converts to naphthalene and dihydronaphthalene as shown in Scheme 1, in which  $\text{R}\cdot$  is a radical fragment generated from pyrolysis of a reactant. The amount of  $\text{H}\cdot$  donated from tetralin to  $\text{R}\cdot$  can be determined by Eq. (1), where  $n_i$  is the moles of species *i*. Fig. S1 shows that little tetralin converts to naphthalene and dihydronaphthalene in the absence of *n*-alkylbenzene, less than 0.8% in 30 min at  $440\ ^\circ\text{C}$ , for example.



## 3. Results and discussion

### 3.1. Quantification of reactive intermediate radicals during pyrolysis of *n*-PrB and *n*-PeB

To cap the primary radicals generated in pyrolysis of the *n*-alkylbenzenes as much as possible, the *n*-alkylbenzenes were pyrolyzed in the presence of different amounts of tetralin at  $440\ ^\circ\text{C}$  for 30 min, the highest temperature and the longest time used in this work. Fig. 3 shows that the pyrolysis of *n*-PeB consumed more tetralin than that of *n*-PrB, suggesting that *n*-PeB generated more radicals than *n*-PrB and the radicals generated abstracted  $\text{H}\cdot$  from tetralin. The consumption of tetralin increases with increasing tetralin/*n*-alkylbenzene molar ratio and approaches asymptotically at a tetralin/*n*-alkylbenzene molar ratio of 4, indicating that this tetralin/*n*-alkylbenzene molar ratio is sufficient to donate  $\text{H}\cdot$  to most of the primary radicals generated.

Fig. 4 shows that the amounts of  $\text{H}\cdot$  donated from tetralin in pyrolysis of *n*-PrB and *n*-PeB at 420 and  $440\ ^\circ\text{C}$  in 5–30 min increase linearly with increasing conversion of these *n*-alkylbenzenes and the relation can be represented by a single slope of 1.8. This indicates that each of the *n*-alkylbenzene molecules pyrolyzed underwent cleavage of one C–C bond and 90% of the radicals generated from the cleavage acquired  $\text{H}\cdot$  from tetralin. Tables 1 and 2 show the quantity of the products observed in the pyrolysis in Fig. 4 from *n*-PrB and *n*-PeB, respectively, and the corresponding  $\text{H}\cdot$  donated from tetralin. In Table 1, the dominant products from *n*-PrB are toluene and  $\text{C}_2$  hydrocarbons (ethane and ethylene) and their quantities are very similar, the minor products are ethylbenzene and methane and their quantities are also very similar. These data indicate that the DP of *n*-PrB involves two routes as shown by Scheme 2(a) and (b), and the dominant route is the cleavage of alkyl  $\beta$  bond in Scheme 2(a) [22]. The small amounts of ethylene may be attributed to the occurrence of Fabuss-Smith-

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