Kinetics of the Thermal Degradation of n-Propylbenzene in a Micro Flow Reactor by Gas Chromatography*

V. Švob and Dj. Deur-Šiftar

INA — Institute for Research and Development
41000 Zagreb, Croatia, Yugoslavia

The kinetics of the thermal degradation of n-propylbenzene was studied by pyrolysis gas chromatography. The sample was pyrolyzed in the gas phase, in a gold capillary tube inserted in the micro flow reactor system that was directly connected to the gas chromatograph. The degradation products were analyzed on a glass capillary column with silicone rubber SE-30 as the liquid phase. The kinetic data was obtained through qualitative and quantitative analysis of the degradation products. The results show that the pyrolysis of n-propylbenzene is a first order reaction with an activation energy of 44.0 kcal**/mol.

INTRODUCTION

Data on accurate measurements of kinetics in the homogeneous gas reactions are few. In general, they are performed in a static way. For higher temperatures and faster reaction rates flow reactors have to be used. The gas chromatographic analysis of the degradation products obtained by pyrolysis in a microreactor can be used for very accurate determination of kinetic data[1]. Tinkelenberg[2] has studied the kinetic characteristics of pyrolysis in gas chromatographic systems and has found that the real kinetic behaviour of microreactors is neither »tank flow« nor »tube flow« but somewhere between these two extremes, depending on the dimensions.

So far Leigh and Szwarc[3] have studied the kinetics of pyrolysis reactions of a number of alkylbenzenes: ethylbenzene[4], n-butylbenzene[5], cumene, t-butylbenzene and p-cymene[6], using the »toluene carrier technique«. Our investigations however, comprise the study on the gas phase pyrolysis of more than 40 alkylbenzenes in the micro flow reactor[7,8,9], including the kinetics of the thermal degradation of n-propylbenzene.

EXPERIMENTAL

A tubular flow microreactor with gold capillary (1119 mm × 1.2 mm i.d.) described by Cramers and Keulemans[10] was used. The reactor temperature was measured by chromel/alumel thermocouple in the core of the reactor and read on a digital voltmeter. The pyrolysis unit was connected to the gas chromatograph directly (in series).

A Becker-Delft gas chromatograph Model 1452 DPF equipped with a flame ionization detector was applied.

An open tubular glass column 25.5 m long and 0.50 mm i. d. with silicone rubber SE-30 as the stationary phase was used.

The quantitative interpretation of the pyrolytic products was performed by the Infotronics CRS 11 HB digital readout system.

The samples were introduced by a »Hamilton« 1 μl syringe equipped with a Chaney adaptor for reproducible injections.

The investigated sample, n-propylbenzene was an API standard sample. Working conditions were the following: column temperature was 65 °C, the carrier gas was helium at a flow rate of 1.5 ml/min, and the splitting ratio was 1 : 67. The experiments were performed with different sample sizes, at different temperatures and reaction times in order to obtain the data necessary for kinetic measurements.

RESULTS

Table I presents the composition of the pyrolysis products of n-propylbenzene, at 595 °C and a reaction time of 20 seconds. The obtained results show that the degradation mechanism is complex and a great number of reactions are included.

TABLE I

Composition of the pyrolysis products of n-*propylbenzene (reaction temperature 595* °*C, reaction time 20 seconds, amount of sample 0,3 μl)*

Products	Composition mol. %	Composition wt. %
Methane	4.0	20.34
Ethane	0.8	2.20
Ethylene	3.3	9.60
Propylene	0.3	0.57
Benzene	1.7	1.79
Toluene	7.3	6.43
Ethylbenzene	2.3	1.79
Styrene	26.5	20.75
i-Propylbenzene	0.3	0.24
Alylbenzene	0.2	0.16
n-Propylbenzene	50.9	34.50
α-Methylstyrene	0.5	0.33
m-Methylstyrene	0.6	0.41
i-Butylbenzene		
sec.-Butylbenzene	0.2	0.08
i-Allylbenzene	0.9	0.65
Indene	0.2	0.16

Plotting the changes of the residence time of n-propylbenzene in the pyrolyzer *versus* the degree of sample conversion a linear relationship, as presented in Fig.1., is obtained. The straight line originating from zero is valid proof that the reaction follows first order kinetics.

The same conclusion is obtained from the study of pyrolytic products composition with respect to the amount of the sample. The main components in the pyrolyzates did not change, and only a slight decrease of conversion (Fig. 2.) could be observed.

The rate constant for the first order reaction can generally be calculated from the equation:

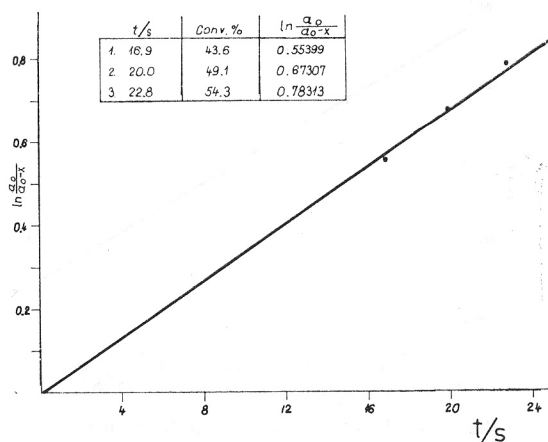$$k\,t = \ln(c_o/c_L) = \ln[1/(1-x)] \qquad (1)$$

	t/s	Conv. %	$\ln\dfrac{a_0}{a_0-x}$
1.	16.9	43.6	0.55399
2.	20.0	49.1	0.67307
3.	22.8	54.3	0.78343

Fig. 1. Plot of $\ln[a_0/(a_0-x)]$ *vs.* reaction time for n-propylbenzene (reaction temperature 595 °C, amount of sample 0.3 µl)
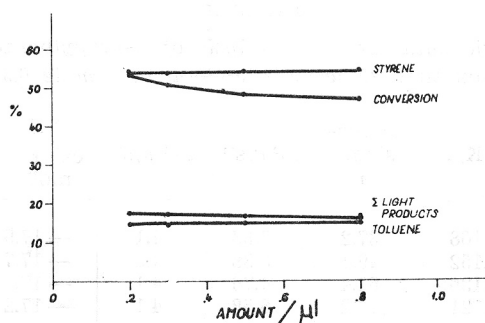

Fig. 2. Conversion and main degradation products of n-propylbenzene dependence on the sample amount (reaction temperature 595 °C, reaction time 20 seconds)

where c_0 is the concentration of the reactant at the reactor inlet,

c_L the concentration of the reactant at the exit, and

x is the fraction of the reactant which reacts.

A plot of $\ln k$ *versus* $1/RT$ yields Arrhenius' plot whose slope gives the activation energy, E_a of the reaction (Fig. 3.). The overall reaction of pyrolysis of n-propylbenzene gives $E_a = 44.0$ kcal/mol.

The frequency factor, k_0 and entropy, ΔS of activation were calculated from the Arrhenius' equation and the equation for absolute reaction rates.

In connection with the increased number of moles during the reaction, the enthalpy of the reaction, ΔH is not equivalent with the activation energy[12]. They are connected by the following term:

$$\Delta H = E_a + n\,RT - RT \qquad (2)$$

where n represents the number of moles of products formed from one mole of reactant.
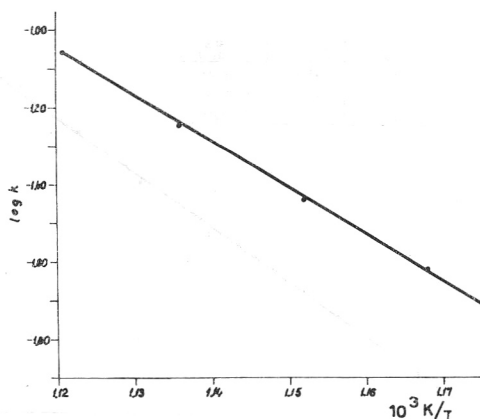
Fig. 3. Arrhenius' plot for n-propylbenzene
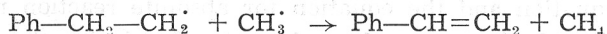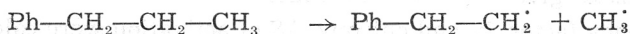
All obtained kinetic data are given in Table II.

TABLE II

Kinetic data for the pyrolysis of n-*propylbenzene*
(reaction time 20 seconds, amount of sample 0.3 µl)

$t/^0C$	T/K	$10^3 K/T$	Conversion, %	$10^2 k/s^{-1}$	$10^{-9} k/s^{-1}$	$\dfrac{\Delta S}{cal\ K^{-1}\ mol^{-1}}$	n/mol	$\dfrac{\Delta H}{kcal\ mol^{-1}}$
583	856	1.168	37.2	2.33	4.1	— 17.9	0.355	42.9
595	868	1.152	49.1	3.38	4.2	— 17.7	0.475	43.1
607	880	1.136	61.4	4.76	4.1	— 17.5	0.594	43.3
619	892	1.121	73.2	6.58	4.1	— 17.2	0.733	43.5

DISCUSSION

From the obtained results it is possible to make a few interesting observations and comparisons with Leigh and Szwarc's paper[3].

Pyrolysis of n-propylbenzene gives 15 different products (Table I) suggesting different reactions during pyrolysis. The main reaction (according to the amount of products) is the breaking of the carbon-carbon bond in γ-position to the phenyl double bond followed by hydrogen transfer.

$$Ph—CH_2—CH_2—CH_3 \quad \rightarrow Ph—CH_2—CH_2^· + CH_3^·$$

$$Ph—CH_2—CH_2^· + CH_3^· \rightarrow Ph—CH=CH_2 + CH_4$$

The initially formed amounts of styrene and methane are practically equimolar. The next reaction evolved during pyrolysis is the breaking of the carbon-carbon bond in β-position. The molar amount of toluene, thus formed is about 1/3 that of styrene. The other reactions are present in lower extent. It might be possible, of course, that during pyrolysis some reactions occur in steps, and a few products originate from them.

In previous work[3] on the pyrolysis of n-propylbenzene, the »toluene carrier technique« was used. The main feature of this method is to trap formed radicals and thus prevent any other reaction. The pyrolysis is performed by introducing the sample (n-propylbenzene) in toluene vapors in the reactor. Toluene forms stable benzyl radicals:

$$Ph—CH_3 \rightarrow Ph—CH_2^{\cdot} + H^{\cdot}$$

which can react with other radicals. Since the resonance energy of benzyl radicals is large, the authors expect that the bond $PhCH_2$—R will be the weakest one in the molecule $PhCH_2R$. Consequently, they suppose the breaking in β-position to the phenyl double bond. The next step of the reaction will be:

$$Ph—CH_2^{\cdot} + {\cdot}H_2C—Ph \rightarrow Ph—CH_2—CH_2—Ph$$
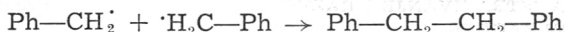
The authors have found an amount of dibenzyl in pyrolysis products but they do not specify either qualitatively or quantitatively all obtained products. We did not obtain dibenzyl as a degradation product.

Due to a quite different approach to the pyrolysis of n-propylbenzene we have got a lower value of E_a (44.0 kcal/mol).

CONCLUSIONS

The kinetics of the pyrolysis of n-propylbenzene in the vapor phase in a micro flow reactor was studied. The composition and the amount of the degradation products were determined. The reaction follows first order kinetics. It was found that the main reaction evolved in pyrolysis is the breaking of the bond in γ-position to the phenyl double bond which is followed by hydrogen transfer. This mechanism disagrees with the findings of Leigh and Szwarc who proposed the breaking of the β-bond. The corresponding differences in kinetic data are also obtained in regard to their investigations.

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IZVOD

Kinetika termičke razgradnje n-propilbenzena u protočnom mikroreaktoru praćena plinskom kromatografijom

V. Švob i Dj. Deur-Šiftar

Promatrana je kinetika pirolitičke razgradnje n-propilbenzena u plinovitoj fazi u protočnom mikroreaktoru. Produkti razgradnje određivani su kvalitativno i kvantitativno plinskokromatografskom analizom. Utvrđeno je da je piroliza n-propilbenzena homogena plinska reakcija prvog reda u kojoj je preferirano cijepanje lateralnog lanca u γ-položaju prema dvostrukoj vezi iz benzenskog prstena. Energija aktivacije reakcije iznosi 44,0 kcal/mol što se, kao i ostali kinetički parametri reakcije, s obzirom na razliku u mehanizmu razgradnje razlikuje od rezultata postignutih primjenom tzv. »toluene carrier« tehnike.