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PYROLYSIS OF BENZENE-NAPHTHALENE MIXTURES: A TEMPERATURE DEPENDENCE STUDY

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ABSTRACT

The pyrolysis of benzene-naphthalene mixtures was carried out in the range of 450-570°C and the principal products were determined. The yields of all the products increase at higher temperatures. A measure of the rates of formation of biphenyl and 1,2'-binaphthyl indicates the occurrence of a slight difference between their activation energies. The presence of alumina in the system has been also investigated.

INTRODUCTION

The pyrolysis of organic systems has been actively studied for many years^{1,2}. In spite of the large amount of work and the progress that has been made, there still remain many areas of uncertainty. Many difficulties, encountered in these works, make seldom incomparable the results obtained in different experiments. However, interest in the pyrolysis of aromatic compounds is high today due to their role in many industrial processes. Furthermore, the gas³ emitted from combustion engines or from industrial combustion contains a number of pollutants which exhibit hazardous effects. The carcinogenity proved or suspected of some polycyclic aromatic hydrocarbons may be mentioned.

Since environmental protection is an important objective, a study of the mechanism of pyrolysis processes can contribute to reduce the formation of hazardous pollutants.

In previous works we investigated the formation of triphenylene⁴ and other polycyclic hydrocarbons⁵ from the pyrolysis of benzene. An approach to understand the mechanism of formation of fluoranthene was carried out by pyrolyzing mixtures containing naphthalene and benzene in different proportions⁶. In fact, the pyrolysis of simple systems such as a binary hydrocarbons mixture allows a relatively easy approach to elucidate the mechanisms involved in the pyrolysis of more complex mixtures. Furthermore, one of the principal products of the pyrolysis of this system is fluoranthene, which occurs in the environmental concentrations considerably greater than those of the more studied benzo(a)pyrene. It is a common environmental pollutant which has been found in used oil⁷, cigarette smoke⁸, and airborne particulates⁹.

In the present work the study of the pyrolysis of a naphthalene-benzene mixture was carried out at different temperatures and the influence of alumina on the system was studied.

EXPERIMENTAL

Known volumes of a solution of naphthalene in benzene (naphthalene molar fraction 0.018) were introduced into 15 mL Pyrex ampoules, which were then sealed under vacuum at liquid nitrogen temperature and placed into a furnace previously heated at the selected temperature. The pyrolysis products were then analysed by a 5890 Hewlett Packard Gas Chromatograph on a 25 m SE 20 capillary column. GC-MS analysis of a pyrolyzed mixture was carried out by a Carlo Erba system.

RESULTS AND DISCUSSION

It was established that C-H aromatic bond breaking occurs near 400°C and generates free radicals¹⁰, while at higher temperatures aromatic rings can also be broken.

Primary phenyl and naphthyl radicals, as well as radicals formed by aromatic ring cleavage, can undergo addition to other molecules present.

The gas-chromatographic analysis was focused on the detection of the following compounds: benzene (PH), naphthalene (NH), biphenyl (PP), isomeric terphenyls (o-T, m-T, and p-T) and phenylnaphthalenes (1-PN and 2-PN), triphenylene (Tr) and fluoranthene (Fl), as well as isomeric binaphthyls (NN). The chromatograms also show the presence of other compounds whose identification was partially achieved by GC-MS.

In Table 1 the yields of the pyrolysis products at 500°C are reported as functions of the amount of solutions and alumina content. It can be observed that in all the experimental conditions the yields of the products do not differ.

Table 1. Yield (µmol L-) of products after 6 hours	pyrolysis at 500°C
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Alumina mg	0	0	23	48
Solution µL	50	100	50	50
PP	1360	1320	1420	1310
o-T	6	7	9	7
m-T	24	19	22	20
p-T	12	15	13	14
1 -PN	16	13	11	11
2-PN	34	41	44	46



Figure 1. Yield of biphenyl (µmol L⁻¹) versus pyrolysis time (hours) at 480°C

The yield of biphenyl linearly increases with the pyrolysis time within the experimental errors (8%) up to 6 hours, as shown by the plot of Figure 1, that obeys to the kinetic equation:

$$[\mathbf{PP}] = \mathbf{k} \mathbf{t}$$

The calculated rate constants for biphenyl and 1,2'-binaphthyl formation are reported in Table 2.

Table 2. Rat	te of formation of	f biphenyl and 1	,2'-binaphthyl in	µmol L ⁻¹ per ho	our	
Product	Alumina	470°C	480°C	510°C	540°C	570°C
РР	no	29	70	337	1298	4633
PP	yes	31	80	317	1188	4375
1,2'-NN	no	< 0.01	0.01	0.9	10	40
1,2'-NN	yes	0.03	0.07	3.1	12	43

It can be observed that in the range of temperatures investigated the yield of biphenyl is not influenced by the presence of alumina in the system, while it acts as a catalyst for naphthalene. We suppose that alumina favours the cleavage of the C-H bond of naphthalene. Other isomeric binaphthyls were formed with lower yields (about 1/3 of the yield of 1,2' isomer).

Together with biphenyl other products coming from the pyrolysis of benzene, namely isomeric terphenyls and triphenylene, have also been found. Their yields with respect to biphenyl are reported in Table 3. Effects of the presence of alumina were not observed within experimental error.

	450°C	480°C	510°C	540°C	570°C
o-T	0.45	0.45	0.41	0.44	0.56
m-T	1.76	1.67	1.69	1.96	1.64
p-T	0.52	1.02	0.87	0.81	0.97
Tr	0.55	0.69	0.55	0.68	0,64

Table 3. Yields (%) of isomeric terphenyls and triphenylene with respect to biphenyl

The presence of naphthalene in the system leads to the formation of isomeric phenylnaphthalenes and fluoranthene, whose yields are reported in Table 4.

	Table 4. Tields of pytolysis products containing the naphthalene ring (76 with respect to oph					
	450°C	480°C	510°C	540°C	570°C	
1-PN	1.32	0.98	1.09	1.15	1.02	
2-PN	4.39	3.97	4.06	3.87	4.51	
Fl	2.99	2.56	2.64	2.34	3.01	

Table 4. Yields of pyrolysis products containing the naphthalene ring (% with respect to biphenyl)

Also in this case the presence of alumina does not influence the yields of the products.

Since the yields of the reported products referred to biphenyl do not vary between temperatures of 450°C to 570°C, the rate of their formation will depend on the primary step of the reaction: the cleavage of the C-H bond of aromatics. The large excess of benzene with respect to naphthalene ensure that the formation of phenyl radicals is the rate determining step of the reaction.

It was previously established that the self-condensation reactions leading to the formation of triphenylene⁴ and fluoranthene⁶ were consecutive processes of aryl radical addition and cyclodehydrogenation. The reported results confirm such a hypothesis. Furthermore, it was suggested⁶ that naphthylation of benzene was a slower process than phenylation of naphthalene. It might be due to a lower reactivity of naphthyl radicals or to a higher energy required for their formation.



Figure 2. Arrhenius plots (ln k vs $10^3/T$) for biphenyl and 1,2'-binaphthyl formation.

From the plots of Figure 2 a rough estimation of the activation energy for biphenyl and 1,2'-binaphthyl formation can be obtained. It can be observed that the activation energy for 1,2'-binaphthyl formation is slightly higher than that one of biphenyl. It can be assumed that it can be due to a higher activation energy for the C-H cleavage in naphthalene than in benzene.

The gas chromatographic analysis showed other peaks than those reported previously. To obtain information about them, a GC-MS was carried out. Some of them were identified, the presence of some alkylarenes, like ethylbenzene and o-ethylmethylbenzene, suggests cleavage of naphthalene ring. The same process, followed to the addition to a benzene molecule, is responsible for the presence of fluorene^{11,12}. The formation of indenofluoranthene agrees with the data reported in the literature².

Other identified products, namely pyrene, anthracene, phenanthrene, dibenzoanthracene, methylbiphenyl, methylphenanthrene, quaterphenyl, can be due to the pyrolysis of benzene⁵ or related to the presence of naphthalene.

To reduce the formation of such products and to study the effect of the presence of alumina, the solution was pyrolyzed at 400°C for 68 hours. The yield of biphenyl obtained in this experiment, 0.049% and 0.169% in the absence and in the presence of alumina, shows that alumina also favours the cleavage of C-H bond in benzene which at higher temperatures occurs without the aid of catalyst.

CONCLUSION

The pyrolysis of benzene-naphthalene mixtures leads to the formation of many products. However the first steps of the reaction are the cleavage of the aromatic C-H bond and the cleavage of the aromatic rings.

The first process leads to the formation of phenyl and naphthyl radicals, the former requiring a lower activation energy. The presence of a catalyst, such as alumina, apparently favours the C-H cleavage of naphthalene more than in benzene over 450°C. However at 400°C its action on C-H benzene bond can not be neglected.

The second process can be explain the formation of many of the compounds identified and seems responsible of the complexity of the gas chromatogram. Owing to the low concentration of these compounds, a quantitation could not be carried out and the influence of the presence of alumina could not be measured.

To clarify the pyrolysis mechanisms, low temperatures in a simple system should be used to distinguish the first reactions steps.

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