ROLE OF ETHYLENE IN FORMATION OF BENZENE BY PYROLYSIS OF n-HEXANE

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Pyrolytic tars are a rich potential source of aromatic hydrocarbons, which make up to 20% of the liquid pyrolysis products of petroleum fractions. In this connection the question about the mechanism of formation of arenes and of benzene in particular is of considerable interest.

It is ordinarily assumed that formation of aromatic hydrocarbons proceeds in at least two steps. First the hydrocarbons initially present break down to C_2-C_4 olefins, and then condensation of olefins leads to aromatic pyrolysis products. Different opinions have been expressed about the intermediate role of the lower olefins in the aromatization reaction. Thus it is suggested in [1] that the main intermediate for the formation of benzene is ethylene, in [2] propylene, in [3] 1,3-butadiene. Much of the data about the mechanism of pyrolysis of individual hydrocarbons, among them low-molecular-weight olefins, is difficult to compare because the investigations were carried out under differing conditions. The main attention was focused on the formation of gaseous products [4-6], whereas the secondary reactions of low-molecular-weight olefins were insufficiently studied.

The goal of the present study is to explain the pathway for formation of benzene on pyrolysis of paraffin hydrocarbons and the participation of ethylene in this reaction. n-Hexane was taken as the starting material because it had been shown in preliminary experiments that its pyrolysis at 800°C proceeds without formation of any hydrocarbons above C_7. Secondary transformations of the intermediately formed ethylene were studied with the aid of labeled molecules, in which a binary mixture of n-hexane and ethylene labeled with ^{14}C was studied.

EXPERIMENTAL

In this work technical n-hexane was used with an impurity of not more than 2.5% isohexane, and ethylene containing $\leq 2\%$ impurities, mainly ethane. Ethylene-^{14}C was obtained by dehydration of ethanol-1-^{14}C over Al_2O_3 at 400°C in a stream of helium.

The pyrolysis was carried out in an impulse radiochromatographic apparatus in a stream of He at 800°C. A quartz tube with a well for a thermocouple served as the reactor. Hydrocarbons were added to the reactor by means of injectors with two connecting devices combined in tandem with spacing providing for simultaneous introduction of the compounds into the reaction zone. The amounts for each impulse were 23 μmoles (3 μl) of n-hexane, 111.6 μmoles (2.5 ml) of ethylene. The contact time varied with both the changes in the flow of the carrier gas and the length of the heating zone. The experiment was carried out at a maximum partial pressure of the hydrocarbons of 55 mm Hg per impulse. The products leaving the reactor were caught in a trap containing Al_2O_3 cooled with liquid nitrogen. For analysis of the sample the trap was heated rapidly, and the products, without separation of the liquid and gas phases, were injected into the chromatograph.

Hydrocarbons were analyzed by a GLC method on three successive columns (Table 1). The amount of H_2 was calculated by the material balance method. The radioactivity of the products was measured by a proportional radioactive flow-type counter located at the exit of the chromatograph.

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TABLE 1. Chromatographic Columns for Analysis of Pyrolysis Products

Hydrocarbons	Phase	Length, m	T, °C
C_1–C_3	Aluminum oxide	3	70
C_4	10% Triethylene-glycol dibutyrate on Celite 545	10	20
$>C_4$	12% Tricresyl phosphate on Celite 545	10	70

DISCUSSION OF RESULTS

The data obtained (Table 2) show that on increased contact time the conversion of n-hexane increases and reaches 97% for a contact time of 2.36 sec. The main products of pyrolysis of n-hexane are ethylene, propylene, CH_4 and H_2. Moreover small quantities of propane, butane, isomeric butenes, pentenes, pentadienes, 1,3-butadiene, cyclopentadiene and benzene were found. With an increasing extent of reaction in the time intervals studied the yield of CH_4, ethylene and benzene increases, but propylene, butenes and 1,3-butadiene go through a maximum and are less evident later on. Significant quantities of benzene appear only when n-hexane is almost absent in the products. This shows that benzene is a secondary product of pyrolysis and it is not formed from the C_6 hydrocarbons but from the lower-molecular-weight products. Among the lower-molecular-weight compounds in high concentration is ethylene. It could be surmised that ethylene is an intermediate product of aromatization.

Benzene forms from ethylene either as a result of the trimerization reaction or by the interaction of ethylene with other molecules or radicals formed from n-hexane. If the first mechanism is applicable pyrolysis of ethylene by itself should yield more benzene than pyrolysis of n-hexane. However data for ethylene transformations (see Table 2) show that it is significantly inferior to n-hexane in its reactivity: For the same contact times when n-hexane conversion is almost complete the conversion of ethylene is only about 9%.

In contrast to n-hexane the main products of ethylene conversion are CH_4 and H_2, which agrees with the data of studies [4-7]. The condensation reaction proceeds slowly, which is indicated by the low yield of propylene, 1,3-butadiene, and benzene. The content of the latter in the pyrolysis products reaches about 0.3 mole % for a contact time of 7.2 sec and for a contact time less than 1.5 sec benzene is essentially not formed. Evidently trimerization of ethylene does not occur and benzene forms by a different mechanism.

TABLE 2. Yields of the Main Products of Hydrolysis of n-Hexane at 800°C

	n-Hexane				Ethylene				
Contact time, sec	0,29	0,58	1,18	2,36	0,75	1,50	3,00	5,00	7,20
% conversion	71,4	83,9	94,6	97,4	5,3	6,1	9,5	13,3	17,0
Mole % of constituents									
Hydrogen	15,9	14,4	9,1	9,7	2,7	3,0	5,1	8,5	11,7
Methane	11,3	15,1	23,4	24,2	3,4	4,3	7,5	11,2	14,8
Ethylene	45,7	48,9	52,3	55,1	92,0	90,7	84,7	77,2	70,5
Acetylene	–	–	–	–	0,5	0,6	0,8	1,0	0,9
Propane	0,5	0,4	0,2	0,2	–	–	–	–	–
Propylene	11,3	11,1	9,1	7,4	0,3	0,4	0,4	0,5	0,5
Butane	0,1	0,2	0,3	0,4	–	–	–	–	–
1-Butene	1,4	1,0	0,3	0,1	–	–	–	–	–
trans-2-Butene	0,6	0,5	0,4	0,2	–	–	–	–	–
cis-2-butene	1,0	0,8	0,4	0,1	–	–	–	–	–
1,3-Butadiene	1,2	1,5	1,6	1,4	1,1	1,1	1,4	1,4	1,4
1-Pentene	0,1	0,1	сл	Сл	–	–	–	–	–
2-Pentenes	0,2	0,1	0,1	Сл	–	–	–	–	–
1,3-Pentadiene	0,2	0,2	0,1	Сл	–	–	–	–	–
Cyclopentadiene	0,1	0,1	0,2	0,3	–	–	–	–	–
Benzene	–	0,4	1,0	1,6	–	сл	0,1	0,2	0,3
n-Hexane	10,5	5,4	1,7	0,8	–	–	–	–	–

TABLE 3. Composition of the Pyrolysis Products of Mixtures of n-Hexane and Ethylene at 800°C

Contact time, sec	0,25	0,50	0,75	1,00
Mole % of constituents				
Hydrogen	13,6	10,6	7,9	10,3
Methane	6,5	13,7	14,9	16,3
Ethane	2,7	2,6	2,5	2,1
Ethylene	64,3	64,8	65,6	61,4
Acetylene	—	0,1	0,8	1,3
Propane	0,2	0,1	0,1	0,2
Propylene	5,9	4,5	3,8	5,4
Butane	0,2	0,2	0,2	0,3
1-Butene	1,5	1,2	0,8	0,7
trans-2-Butene	0,1	0,1	0,1	0,1
cis-2-Butene	Trace	0,1	0,1	0,1
1,3-Butadiene	1,4	1,5	1,6	1,6
Pentenes	0,1	0,2	Сл	—
n-Hexane	3,2	2,3	1,0	0,4
Cyclopentadiene	0,1	0,2	0,2	0,3
Benzene	0,2	0,2	0,3	0,5

To determine the role of ethylene in the formation of benzene we investigated the pyrolysis of a binary mixture of n-hexane and ethylene labeled with ^{14}C in 1:3 mole ratios.

In [8, 9] it was shown that pyrolysis of ethane, propane and butane in a mixture with unsaturated hydrocarbons increases the rate of decomposition of the latter. In agreement with our data (Fig. 1) the conversion of ethylene in the presence of n-hexane increases approximately threefold, and the yields of benzene and ethylene increase significantly in the process. Thus for a contact time of 0.75 sec a substantial amount of benzene containing the radioactive label appears in the pyrolysis products of the binary mixture, whereas pyrolysis of ethylene by itself under these conditions does not form any benzene. This could explain why on pyrolysis of the mixture for even short periods of contact time in the reaction zone, products of decomposition of n-hexane appear that are capable of interaction with ethylene with conversion into benzene.

Results of pyrolysis experiments with the n-hexane—ethylene-^{14}C mixture show that the main products of transformation along with CH_4 and H_2 are likewise propylene and 1,3-butadiene. Furthermore, benzene and the C_2–C_5 hydrocarbons are present in low concentrations. As in the experiments with n-hexane by itself, increasing the contact time leads to increases in the CH_4 and benzene concentration, yields of propylene and butenes reach a maximum, and the concentration of 1,3-butadiene levels off. From the data of Tables 2 and 3 it follows that benzene and CH_4 are the end products of the reaction. One could not say that about 1,3-butadiene because the concentration relationships obtained for it have a character typical of intermediate products. Propylene and butenes evidently, are also intermediate products and in the pyrolysis process are subjected to extensive transformation.

From the data of Fig. 2 it is evident that increasing contact time leads to a notable decrease in the molar radioactivity (MRA) of ethylene. This is explained by the fact that the starting ethylene is diluted by the unlabeled kind formed from n-hexane. Along with this the radioactivity from the ethylene goes over to other reaction products including benzene. This is evidence of the direct participation of ethylene in benzene formation. The MRA curve for benzene changes in a symbatic manner just as that of ethylene. On extrapolation to zero contact time the MRA for benzene approaches 150-180%. From this it follows that in the formation of the aromatic ring not only does one ethylene enter in the reaction, but more, in the limiting instance, two.

The labeled ethylene also participates in the formation of 1,3-butadiene which is verified by the presence of radioactivity in the latter. However since the radioactivity of 1,3-butadiene is very close or a little lower than that of ethylene, it follows that not more than one molecule of labeled ethylene participates in the formation of 1,3-butadiene. It can be assumed that such a result would be obtained if some part of the 1,3-butadiene is formed entirely from the n-hexane.

If it is assumed that benzene is formed from ethylene and 1,3-butadiene, then its MRA should be equal or greater than the sum of the molar radioactivities of these hydrocarbons.

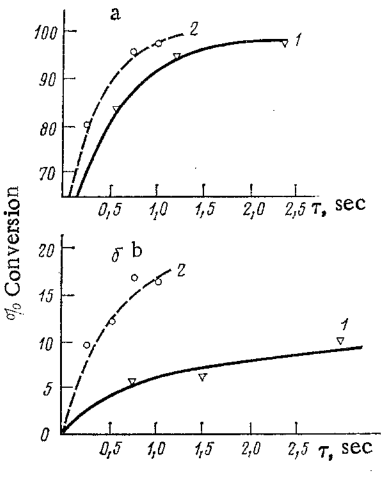


Fig. 1

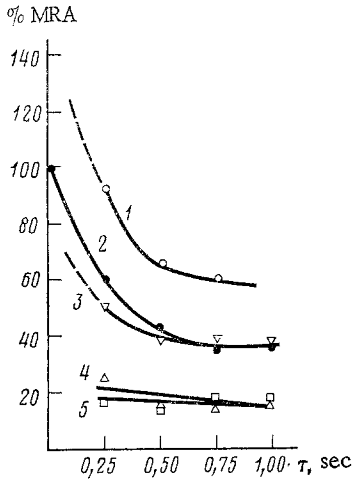
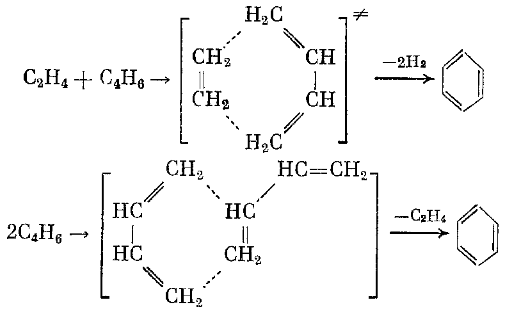


Fig. 2

Fig. 1. Dependence of conversions (a) of n-hexane and (b) of ethylene on the contact time: 1) pyrolysis of individual hydrocarbons; 2) pyrolysis of hexane—ethylene-^{14}C mixtures.

Fig. 2. Dependence of the moles of radioactive pyrolysis products of the n-hexane—ethylene-^{14}C mixture on the contact time: 1) benzene; 2) ethylene; 3) butadiene; 4) propylene; 5) 1-butene.

If the aromatization reaction is brought about by the dimerization of 1,3-butadiene, then the MRA of benzene should not be lower than 1.5 times the MRA of 1,3-butadiene. From the data obtained it is evident that the MRA of benzene is less than the sum of the MRA's of ethylene and 1,3-butadiene, but greater than 1.5 times the MRA of 1,3-butadiene. For this reason it could be assumed that both pathways are probable, and that benzene is formed both by the interaction of ethylene and 1,3-butadiene and by the dimerization of 1,3-butadiene [6].



Among the products of the binary mixture comparable in quantity with 1,3-butadiene are propylene and 1-butene. It could be assumed that these olefins also participate in the aromatization reaction. However as is evident from the data obtained, their MRA's are about 20% of the MRA of the starting ethylene. So the low value of the MRA's of propylene and 1-butene makes it impossible to attach any great significance to their MRA's in the formation of benzene, and consequently, under these conditions the hydrocarbons in question do not make a substantial contribution to the aromatization reaction. However the results obtained do not give a basis for complete elimination of the pathway involving participation of the C_3-C_4 olefins. Most probably these hydrocarbons are also participants in the aromatization reaction and also like ethylene can react with other radicals or molecules with formation of higher-molecular-weight compounds including benzene.

CONCLUSIONS

1. We investigated the thermal transformations of n-hexane, ethylene and a mixture of n-hexane—ethylene-^{14}C at 800°C and partial pressures of the starting hydrocarbons not more than 55 torr. We established that the conversion of ethylene in the presence of n-hexane is substantially increased.

2. The data obtained make it possible to assume that in the pyrolysis of n-hexane the ethylene being formed is involved in the formation of aromatic hydrocarbons, by interacting with radicals or with molecules capable of reacting, in particular with 1,3-butadiene.

LITERATURE CITED

1. K. N. Ivanov and K. E. Masal'skii, Current Concepts about the Chemistry and Kinetics of Pyrolysis Processes [in Russian], Tbilisi (1972).
2. N. A. Sokova, M. F. Polubentseva, V. G. Lipovich, and I. V. Kalechits, Neftepererab. Neftekhim., No. 1, 34 (1972).
3. Yu. G. Kambarov, D. A. Burdzhaliev, and M. A. Dalin, Azerb. Neft. Khoz., No. 9, 40 (1967).
4. T. Kunuqi, T. Sakai, K. Soma, and J. Sasaki, Ind. Eng. Chem., 8, 374 (1969).
5. Yu. P. Yampol'skii, A. M. Brodskii, R. A. Kalinenko, and K. P. Lavrovskii, Neftekhimiya, 4, 691 (1964).
6. R. Z. Magaril, Mechanism and Kinetics of Homogeneous Thermal Transformations of Hydrocarbons [in Russian], Moscow (1970).
7. R. E. Kinney, D. J. Growley, Ind. Eng. Chem., 46, 258 (1954).
8. R. A. Kalinenko, E. N. Avdeeva, N. S. Nametkin, Neftekhimiya, 18, 217 (1978).
9. O. V. Kal'nitskii, G. V. Tuchkov, E. A. Silkin, and T. A. Chulyukova, Khim. Prom., 739 (1977).

OXIDATIVE SPLITTING OF SECONDARY CYCLOALKANOLS BY $Pb(OAc)_4$—LiCl AND $Pb(OAc)_4$—$Cu(OAc)_2$ SYSTEMS

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In the reaction of tertiary cyclic alcohols with oxidizing systems based on lead tetraacetate (LTA), oxoalkyl radicals $RCO(CH_2)_2\dot{C}H_2$ (n = 2-5) are formed, which in a LTA—$Cu(OAc)_2$ system quantitatively transform into ω-unsaturated ketones as the result of oxidative deprotonation [1], while in the LTA—metal halide system they become oxidized to ω-haloalkanones [2].

Information on the reaction of secondary cyclic alcohols with LTA proceeding with ring opening is limited. It is known that for cyclobutanol, the contribution of the decyclization reaction (β-fragmentation) of cyclobutoxyl radicals formed at the first stage to the overall transformation process is ∿15%. During oxidation with LTA, secondary cycloalkanols with C_5-C_{16} ring size convert mainly into cyclic ketones; the amount of β-fragmentation products does not exceed ∿1.5-4%. If due to structural features of the cycloalkoxyl radicals, their rearrangement with 1,5- or 1,6-migration of the hydrogen atom is possible, then epoxycycloalkanes, products of intramolecular oxidative cyclization, are formed [3].

To prepare ω-formylalkyl radicals $\dot{C}H_2(CH_2)_{n+1}CHO$ (n = 2, 3) and to study their oxidative transformations, in the present work we oxidized cyclopentanol and cyclohexanol by LTA—LiCl and LTA—$Cu(OAc)_2$ system. The reactions were carried out at 65-80°C in benzene in the presence of pyridine (∿1 mole per mole of LTA) to complete conversion of LTA.

Table 1 lists the oxidation products of cyclopentanol and cyclohexanol by the LTA—LiCl system, and Table 2 the oxidation products of these alcohols by the LTA—$Cu(OAc)_2$ system. Their formation can be represented by the following scheme:

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