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Chemistry

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Abstract

Full Text

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On the Effect of Local Activation in the Low-Temperature Pyrolysis of Anthracene and Bianthryl

(Presented by Academician V. N. Kondrat’ ev, February 21, 1964)

It was reported earlier that paramagnetic polymers with a conjugated system arise during the thermal treatment of aromatic compounds, including anthracene ([1]-[4]). Along with this, it was established that paramagnetic polymers formed in various polymerization reactions, or specially added to diamagnetic substances with a system of π—π conjugation, are highly effective specific activators, apparently increasing the probability of the singlet-triplet (S—T) transition in the activated complex and thereby stimulating a number of chemical transformations of polyconjugated systems (the “local-activation” effect) ([1]-[7]).

In the present work we report on the influence of paramagnetic polymers (PP) on the low-temperature pyrolysis of anthracene (A) and bianthryl. The choice of bianthryl as the second object is explained by the fact that this hydrocarbon is usually formed in the pyrolysis of A and has a lower excitation energy.

Starting substances: A, “synthetic for scientific work” grade, with m.p. 216°; bianthryl with m.p. 308°. Preliminary experiments on the pyrolysis of A at 450° in a stainless-steel autoclave showed that the dynamics of gas evolution (Fig. 1) correspond to the autocatalytic character of the process.

Fig. 1. Increase in gas pressure during anthracene pyrolysis (450°)

All further work was carried out in glass ampoules filled to 15% of their volume. The filled ampoules were evacuated for 6-8 hours at 10^{-5} mm Hg, sealed off, and heated at $450 \pm 3°$. The amount of gases evolved was determined from the pressure in an ampoule opened at $\sim 20°$; the gas composition was determined mass-spectrometrically; the concentration of paramagnetic particles in the solid residue was determined on an EPR-2 radiospectrometer, the signal in all cases being a narrow symmetric singlet. Thin-layer chromatography on alumina was used to study the benzene-soluble portion of the solid residue.

The results obtained in pyrolysis from 45 min to 4 h 20 min are shown in Figs. 2 and 3. Noteworthy is the fact that the onset of a sharp increase in gas

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Figure 2

Figure 2: Figure 2

evolution between 1 and 2 h of heating coincides in time with the rise of the paramagnetism curve characteristic of autocatalytic processes. All this supports the specific catalytic action of the PP formed in the pyrolysis process itself. At the beginning of gas evolution, only hydrogen is formed in very small amounts; then, apparently under the influence of PPs, cracking and hydrogenation processes are induced, as a result of which the amount of light aliphatic hydrocarbons increases sharply. The solid residue after pyrolysis for up to 1-1.5 h is practically completely soluble in benzene; with an increase in the duration of heat treatment the solubility decreases (see also (4)). At the same time as the total concentration of paramagnetic particles in the solid residue continuously increases with increasing heating time, the paramagnetism of the benzene-soluble part of the residue reaches a maximum at ~ 2 h of heating and then decreases as a result of the transition of PPs into an insoluble state. From the benzene solution, dihydroanthracene and bianthryl were chromatographically isolated and identified by R_f and spectrophotometrically; these are probably among the primary products of the transformation of A. Other substances appearing on the chromatogram were not identified. The amount of dihydroanthracene increases with increasing pyrolysis time up to 2 h and thereafter remains practically constant. The amount of bianthryl at first increases, and after 2 h of heating decreases, which is associated with the high rate of its conversion into soluble and insoluble PPs. Indeed, 45-min pyrolysis of bianthryl led to the formation of an almost completely insoluble paramagnetic polymer.

Fig. 2. Amount of gases evolved in the process of anthracene pyrolysis (moles of gas per mole of anthracene). Traces of ethylene and butadiene were found in all samples. **1** —total amount of gases, **2** —methane, **3** —hydrogen, **4** —ethane, **5** —propane.

Comparative experiments were carried out under identical conditions on pyrolysis for 45 min of A, bianthryl, and A with the addition of 1% of the paramagnetic polymer fraction. The latter was isolated from the products of 2-h pyrolysis of A at 450° by dissolution in benzene and precipitation with methanol; it had an average molecular weight of about 1000 and a concentration of paramagnetic particles of $5 \cdot 10^{17}$ spins/g. The paramagnetic fraction was introduced into A by joint dissolution in benzene followed by removal of the solvent at 20° in vacuum. The results of these experiments are given in Table 1. During this time only a very insignificant amount of H_2 and PPs was formed. The addition of 1% of the paramagnetic fraction not only sharply affected the rate of formation of new amounts of PPs, but also contributed to a sharp acceleration, deepening, and even change in the direction of pyrolysis of A. From the data of Table 1 it is evident that in this case already in the first stage of pyrolysis there is formed—

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Table 1

Initial substance	Anthracene	Anthracene + 1% paramagnetic fraction	Bianthryl
A.* Hydrogen	3.4	24	148
Methane	Not detected	12	124
Ethane + ethylene	»	11	36
Propane	»	15	30
Propylene	»	11	Traces
Butane		17	»
Butadiene		7	»
Total	3.4	97	342
B.** Before heat treatment	$< 10^{14}$	$5 \cdot 10^{15}$	$< 10^{14}$
After heat treatment	$< 10^{14}$	$2 \cdot 10^{17}$	$3 \cdot 10^{18}$

* Gases evolved during chemical treatment (45 min, 450°). Amounts are given in millimoles per mole of anthracene or 0.5 mole of bianthryl.

** Paramagnetism of the solid phase (spins/g).

more than 30 times larger amounts of gaseous products are formed, and these include not only hydrogen and saturated hydrocarbons, but also ethylene, propylene, and butadiene (about 30% of the total amount). It should be noted that the formation of such significant amounts of unsaturated hydrocarbons is not observed even during prolonged pyrolysis of A (see Fig. 2). In this case the solid residue contains a considerable amount of brown oily liquid products, whose chemical nature has not yet been investigated. It differs noticeably from the residue containing the same amount of PP obtained without the introduction of soluble PP from outside. Apparently, the effect of the soluble PP fraction introduced from outside before the beginning of heat treatment, and of the mixture of PP formed during the pyrolysis of A, is different. It also follows from the data in Table 1 that, during the pyrolysis of bianthryl, the rate and depth of thermal destruction, as well as the rate of PP formation, are considerably higher than in the case of A. However, in this case as well the PP formed during heat treatment do not favor the formation of unsaturated hydrocarbons.

Fig. 3. Growth of the concentration of paramagnetic particles (spins/g) during the pyrolysis of anthracene

The observed facts can be explained on the basis of the concepts developed by one of us concerning the effect of local activation and induced reactivity.

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Fig. 3. Growth of the concentration of paramagnetic particles (spins/g) during the pyrolysis of anthracene

Figure 3: Fig. 3. Growth of the concentration of paramagnetic particles (spins/g) during the pyrolysis of anthracene

During the pyrolysis of A without the introduction of PP, for 1-1.5 h only a slight evolution of H_2 is observed, an increase in the number of paramagnetic particles to $3–5 \cdot 10^{15}$ spins/g, and a monotonic increase in the amounts of dihydroanthracene and bianthryl.

Evidently, disproportionation processes occur here, leading to the formation of bianthryl and dihydroanthracene

$$\text{anthracene} \xrightarrow{E} \text{dihydroanthracene} + \text{bianthryl} \tag{I}$$

After 2 h of pyrolysis the amount of dihydroanthracene remains practically constant; the amount of bianthryl decreases, which is apparently associated with the conversion of the latter into polymeric diamagnetic (DP) and paramagnetic products, with the evolution of hydrogen

$$\text{bianthryl} \xrightarrow[-H_2]{E} \text{polymeric diamagnetic products (DP)}$$

$$\text{bianthryl} \xrightarrow{-H_2} \begin{cases} \text{polymeric diamagnetic products} & \text{(DP)} \\ \text{paramagnetic products} & \text{(PP)} \end{cases} \tag{II}$$

The PP that are formed increase the probability of an $S—T$ transition of aromatic hydrocarbon molecules complexing with them (8–10), owing to

which accelerates the process of formation of bianthryl, as well as its conversion into DP and PP

$$2\,\{\mathrm{PP_{soln}}\} \xrightarrow{E} 2 \cdot \mathrm{A}^{\bullet} \xrightarrow{-\mathrm{H_2}} \mathrm{A} - \mathrm{A} \tag{III}$$

$$\{\mathrm{PP_{soln}}\} \xrightarrow{-\mathrm{H_2}} \mathrm{A} - (-\mathrm{A}-)_n - \mathrm{A} \xrightarrow[-\mathrm{H_2}]{} \begin{matrix} \mathrm{DP} \\ \mathrm{PP} \end{matrix} \tag{IV}$$

Activation of PP in polymerization and destructive processes accounts for the autocatalytic character of the accumulation of polymeric and gaseous products (7).

When soluble PP is introduced into A, a π-complex is formed immediately, in which the probability of an $S—T$ transition of A molecules is increased. The predominant process at the initial stage will evidently be (III). Consistent with this is the absence of an induction period in the evolution of hydrogen. At the same time, process (I) occurs, which explains the presence of dihydroanthracene in the solid residue. The introduction of soluble PP (PP_{soln}) also activates process (IV), as is confirmed by the data on paramagnetism and gas formation.

The specificity of the action of soluble PP introduced into A at the beginning of the process, as compared with those formed during pyrolysis, may evidently be due, on the one hand, to a change in the chemical nature of the introduced PP during their heat treatment and, on the other hand, to a different chemical nature of the aromatic molecules complexing with them. In this case the most favorable conditions are created for the hydrogenation and destruction of aromatic nuclei, with the evolution of considerable amounts of saturated and unsaturated hydrocarbon gases.

In the case of pyrolysis of bianthryl, transformations of types (II) and (IV) probably occur already at the beginning of the process, leading to rapid accumulation of soluble and insoluble DP and PP.

The study of the influence of local activation on the mechanism and kinetics of pyrolysis is continuing.

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