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Chemical Reactions of Coal Tar Pitch with Model Organic Compounds

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Abstract

Thermal reactions proceeding through hydrogen transfer from the polyaromatic compounds of coal tar pitch to model organic compounds (nitrobenzene, chlorophenols, and chloraniline) are investigated. Within the temperature range 270–360 °C, there is a complete conversion of nitrobenzene into aniline (with a yield of 75–82 %) and condensation products remaining in the pitch. It was found that 4-chlorophenol enters hydrodechlorination starting at a temperature of 300 °C and leading to the formation of phenol and condensation products. The reactivity of di- and tri-chlorophenols is higher than that of 4-chlorophenol. The features of the reactions are compared using coal tar pitch and hydroaromatic compounds as hydrogen donors.

Keywords: coal tar pitch, hydrogen transfer, polycondensation, nitrobenzene, aniline, chlorophenols, hydrodechlorination

INTRODUCTION

Coal tar pitch, a distillation residue from processing coal tar formed in the production of metallurgical coke, is a complicated system of condensed aromatic compounds with a broad distribution over molecular masses [1–6]. Thermal transformations of polycyclic aromatic hydrocarbons in coal tar pitch at increased temperatures lead to the carbon residue in a high yield. Availability and low cost of coal tar pitch define its promising nature as a raw material not only for use as a binder and impregnating material in the production of carbon-graphite materials and carbon-carbon composites but also as a material to make carbon sorbents, mesophase microspheres, carbon foam, electrode materials for chemical sources of electric energy [6]. An essential factor is the stable chemical composition of coal tar pitch, which is represented mainly by polycyclic aromatic hydrocarbons, good precursors for graphite-like structures.

The complicated chemical composition of coal tar pitch, co-existence of the liquid, liquid crystal (mesophase) and solid (carbon) phases during its carbonization hinder identification and investigation of thermal chemical reactions participated by polycyclic aromatic hydrocarbons that form the basis of coal tar pitch [7].

It is stressed that carbonization of aromatic compounds, by the example of anthracene within temperature range 465–525 °C, starts from hydrogen transfer and condensation (polymerization) of free radicals into the compounds with high molecular mass [8]. Because of this, investigation of the reactions of hydrogen transfer participated by coal tar pitch is significant both for better understanding its carbonization and for its modification using the chemical route.

It was established in the studies of pyrolysis of high-molecular organic compounds in the presence of coal tar pitch that at a temperature up to 400 °C, hydrogen transfer occurs from the compounds of coal tar pitch to the intermediate radi-

cal products of the thermal destruction of the polymer [9–15] and to the unsaturated compound, for example styrene during polystyrene decomposition [15], which initiates reactions in the pitch. Polycondensation in coal tar pitch during the thermal destruction of polystyrene was described previously in the patent [16]. Hydrogen transfer at relatively low temperatures (320–400 °C) from polycyclic aromatic compounds turned out to be an unexpected process. Active donors of hydrogen are hydroaromatic compounds of pitch, such as tetraline, dihydroanthracene, providing hydrogen transfer to the reacting compound with the formation of stable aromatic compounds, naphthalene and anthracene (reverse radical disproportionation [17]).

The goal of the present work was to study the possibility of hydrogen transfer from the aromatic compounds of coal tar pitch to the model organic compounds – nitrobenzene, chlorophenols and chloroaniline. The reactions of these compounds with dihydroaromatic compounds were studied previously in [18, 19].

EXPERIMENTAL

For experiments and for the development of the gas chromatographic procedure of quantitative analysis, we used nitrobenzene, aniline, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and 4-chloroaniline of reagent grade (the content of the major component was not less than 95 %). The characteristics of the samples of industrial coal tar pitch used in the work are listed in Table 1.

Interaction carried out in ampoules

Glass ampoules 3 ml in volume were used to load 0.7 g of a mixture of coal tar pitch with diphenyl (as an internal standard) at a ratio of 100

: 1 and a weighted portion of nitrobenzene of 0.014–0.016 g ($(1.1–1.3) \cdot 10^{-4}$ mol), then the ampoules were blown with argon. In the experiments with chlorophenols and chloroaniline, we used 0.5 g of a mixture of coal tar pitch with diphenyl and 0.025 g of the initial compound ($1.94 \cdot 10^{-4}$ mol of 4-chlorophenol, $1.53 \cdot 10^{-4}$ mol of 2,4-dichlorophenol, $1.27 \cdot 10^{-4}$ mol of 2,4,6-trichlorophenol).

The ampoules were sealed and loaded into a muffle heated to the necessary temperature, then they were kept for a definite time. After cooling to the room temperature, the ampoules were opened and placed (together with the contents) into conical flasks 100 ml in volume, in which 20–30 ml of methylene chloride were present. After 24 h, the ampoules were taken out of the solution, 20–30 ml of isopropyl alcohol were added to the flasks, then the flasks were put on the magnetic mixer to be mixed for 30 min. Then the solution was filtered through a red tape filter and analyzed by means of gas chromatography (GC) with a flame ionization detector (GC-FID) and mass spectrometry (GC-MS).

Experiments under dynamic conditions

These experiments were carried out by passing 10 g of a mixture of toluene and nitrobenzene at a mass ratio of 43 : 57 or 4.8 g of nitrobenzene ($390 \cdot 10^{-4}$ mol nitrobenzene) for 30 min through a metal reactor, with a propeller blade mixer, in which 60 g of coal tar pitch was placed. The height of the pitch layer was 50 mm. Liquid products condensed after the reactor and the residue in the reactor were weighted. Aniline and nitrobenzene concentrations in reaction products were determined by means of GC using toluene as an internal standard.

Reaction products were identified with the help of a Trace GC Ultra DSQ II gas chromatograph–mass spectrometer (USA) (GC-MS condi-

TABLE 1

Characteristics of coal tar pitch

Sample	Parameters according to GOST				Elemental analysis					
	T_p , °C	α , %	α_1 , %	V^g , %	C	H	N	S	O	H/C atomic ratio
Medium-temperature	68	27.0	5.0	59.0	91.9	4.3	1.8	0.6	1.4	0.56
High-temperature	86	34.0	8.1	55.0	93.7	4.0	2.4	–	–	0.51

Note. Here and in Table 4: 1. T_p is softening temperature according to the Ring and Rod method; α is mass fraction of toluene-insoluble substances; α_1 is the mass fraction of quinoline-insoluble substances; V^g is the yield of volatile substances at 850 °C. 2. Dash means that the measurements were not carried out.

tions) with a quadrupole mass spectrometric detector and a quartz capillary column Thermo TR-5ms (polydimethylsiloxane, 5 mass % of phenyl groups), 30 m long, 0.25 mm in diameter, the film thickness was 0.25 mm. The column temperature was: initial – 40 °C (exposure for 3 min), programmed rise with a rate of 10 °C/min to 290 °C (exposure for 30 min), evaporator temperature – 250 °C, source temperature – 200 °C, transition line temperature – 250 °C. The carrier gas was helium, the flow partition was 1 : 50, the flow rate through the column 1.0 mL/min. Scanning was in the mode of electron ionization (70 eV) over total ion current (TIC) with mass range 20–1000 Da.

The quantitative analysis using the internal standard was carried out with the help of a Shimadzu GC 2010 gas chromatograph (Japan) with a flame ionization detector (GC-FID conditions), a quartz capillary column ZB-5 (polydimethylsiloxane, 5 mass % of phenyl groups), 30 m long, 0.25

mm in diameter, film thickness 0.25 mm. Column temperature: initial – 40 °C (exposure for 3 min), programmed rise at a rate of 10 °C/min up to 280 °C (exposure for 30 min), evaporator temperature was 250 °C, detector temperature was 300 °C. Carrier gas was nitrogen, flow partition 1 : 30, the flow rate through the column 1.0 mL/min.

RESULTS AND DISCUSSION

Nitrobenzene hydrogenation

Results of nitrobenzene thermolysis in coal tar pitch in ampoules are listed in Table 2. The only product of hydrogen transfer from coal tar pitch to nitrobenzene, detected with the help of GC, was aniline. Its yield within temperature range 270–360 °C was 75–82 % with the complete conversion of nitrobenzene. The rest part of nitrobenzene (18–25 %) is transformed into condensed products, as experiments in the dynamic mode demonstrated.

When nitrobenzene is passed through a layer of coal tar pitch, the reaction proceeds at a boundary between the gas (nitrobenzene vapour) and liquid (pitch melt) phases. Liquid reaction products condensed after the reactor contain unreacted nitrobenzene, aniline, water and volatile compounds of coal tar pitch. It follows from the data shown in Table 3 that the yield of aniline with respect to reacted nitrobenzene is 67–75 % at 270–300 °C, the amount of water corresponds to the amount of aniline, 25–33 % of nitrobenzene is transformed into nonvolatile products remain-

TABLE 2

Hydrogenation of nitrobenzene by hydrogen transferred from coal tar pitch (experiments in ampoules)

Temperature, °C	Time, min	Nitrobenzene conversion, %	Yield, %	
			Aniline	Condensation products
270	15	100	82	18
300	15	100	75	25
300	30	100	79	21
360	15	100	79	21

TABLE 3

Hydrogenation of nitrobenzene with hydrogen transferred from coal tar pitch (dynamic mode)

Exp. No.	Temperature, °C	Nitrobenzene supplied to the reaction, g (mol)	Products, g (mol)		Selectivity, %		Nitrobenzene conversion, %
			Nitrobenzene	Aniline	Aniline	Condensation products	
1	270	5.7 ^a (463 · 10 ⁻⁴)	1.3 (106 · 10 ⁻⁴)	2.5 (268 · 10 ⁻⁴)	75	25	77
2	300	5.7 ^a (463 · 10 ⁻⁴)	0.8 (65 · 10 ⁻⁴)	2.5 (268 · 10 ⁻⁴)	67	33	86
3	360	4.7 ^a (382 · 10 ⁻⁴)	0.6 (49 · 10 ⁻⁴)	1.5 (161 · 10 ⁻⁴)	48	52	84
4	300	4.8 (390 · 10 ⁻⁴)	1.0 (81 · 10 ⁻⁴)	2.1 (225 · 10 ⁻⁴)	72	28	79
5	300	4.8 (390 · 10 ⁻⁴)	2.7 (219 · 10 ⁻⁴)	0.9 (97 · 10 ⁻⁴)	57	43	44

Note. Experiments 1–4 were carried out using medium-temperature pitch, experiment 5 – high-temperature pitch.

^a A mixture with the mass ratio toluene / nitrobenzene = 43 : 57 was supplied.

TABLE 4

Characteristics of coal tar pitch after passing nitrobenzene (dynamic mode)

Exp. No.	Parameters according to GOST 10200-83				H/C atomic ratio
	T_p , °C	α , %	α_1 , %	V^s , %	
1	Above 170	55	38	47	0.54
2	Above 170	55	—	46	0.54
3	161	50	42	49	0.54
5	—	—	—	—	0.49

Note. For designations, see Table 1.

ing in the reactor as a result of condensation reactions. Selectivity with respect to condensation reactions increases with an increase in reaction temperature and is equal to 52 % at 360 °C. The amount of the formed water corresponds to the amount of aniline.

When the coal tar pitch of V grade (high-temperature) characterized by a higher C/H ratio and a lower amount of active hydrogen is used, nitrobenzene conversion decreases, and the fraction of condensation reactions with its participation increases.

The characteristics of the coal tar pitch after passing nitrobenzene through it are listed in Table 4. The H/C ratio after reaction with nitrobenzene decreases as a consequence of hydrogen transfer from pitch to reaction products, aniline and water. Insufficient accuracy of elemental analysis does not allow us to make a conclusion

concerning changes in nitrogen content in the coal tar pitch after the reaction. An increase in the content of compounds insoluble in toluene and quinoline, along with a decrease in the yield of volatile substances, provides evidence that condensation reactions initiated by hydrogen transfer proceed in the coal tar pitch. The amount of hydrogen transferred from coal tar pitch to the formation of aniline and water in experiments 1 and 2 is about 3 mg ($1.7 \cdot 10^{-4}$ mol) per 1 g of the coal tar pitch.

Hydrodechlorination of chlorophenols and chloroaniline

Results of hydrodechlorination of 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and 4-chloroaniline are presented in Table 5. Hydrodechlorination of 4-chlorophenol with the formation of phenol starts at a temperature of 300 °C, simultaneously, similarly to nitrobenzene hydrogenation due to hydrogen transfer from coal tar pitch, condensation products are formed that cannot be identified by means of GC. Total conversion of 4-chlorophenol within temperature range 300–360 °C reaches 97–98 % at 330 C, selectivity with respect to phenol is 68–88 %.

2,4-Dichlorophenol and 2,4,6-trichlorophenol are more reactive and were not detected in reaction products at 300 °C. The major product of hydrodechlorination of these compounds at 360 °C is phenol, at 300 °C reaction products con-

TABLE 5

Dehydrochlorination of chlorophenols and chloroaniline in coal tar pitch (experiments in ampoules)

Compound	Temperature, °C	Time, min	Conversion, %	Selectivity, %		
				Phenol/aniline ^a	2-Chlorophenol ^b	Condensation products
Chlorophenol	270	15	0	—	—	—
«	300	15	20	40	—	60
«	300	60	90	71	—	29
«	330	30	97	68	—	32
«	360	30	98	88	—	12
Dichlorophenol	300	60	100	19	50	31
«	360	60	100	88	5	7
Trichlorophenol	300	60	100	3	58	49
«	360	60	100	61	—	39
Chloroaniline	300	60	0	—	—	—
«	360	60	100	74	—	26

Note. Dash means that measurements were not carried out.

^a The product of aniline dehydrochlorination.

^b The product of di- and trichlorophenol dehydrochlorination.

tain substantial amounts of 2-chlorophenol, which is less reactive than 4-chlorophenol.

As shown in [18], 4-chloroaniline behaves similarly to 4-chlorophenol and is hydrodechlorinated into aniline with the side formation of condensation products.

Comparison with the reactions of hydrogen transfer from dihydroaromatic compounds

The activity of coal tar pitch in reactions with hydrogen transfer, such as nitrobenzene hydrogenation into aniline and hydrodechlorination of 4-chlorophenol, 2,4-dichlorophenol and 4-chloroaniline with the formation of phenol and aniline, is comparable with the activity of dihydroanthracene, a classical donor of hydrogen.

In nitrobenzene hydrogenation in ampoules, the half-time of the reaction was 80 min at 255 °C and 16 min at 275 °C with dihydroanthracene, 22 min at 300 °C in tetraline [19]. Complete conversion of nitrobenzene in reaction with coal tar pitch is achieved at 270 °C within 15 min.

As described in [18], with the reaction carried out in ampoules at 352 °C for 3 h, the yield of phenol from 4-chlorophenol in dihydroanthracene was 25 %, from 2,4-dichlorophenol – 21 % for 2-chlorophenol and 79 % for phenol, the yield of aniline from 4-chloroaniline was 31 %.

Changes of coal tar pitch characteristics after participation in hydrogen transfer reactions

Changes of the characteristics of coal tar pitch after hydrogen transfer from it to nitrobenzene are depicted in Table 4. The loss of hydrogen causes a decrease in the atomic ratio of H/C in the coal tar pitch, at the same time softening temperature increases, so does the content of α - and α_1 -fractions; the yield of volatile substances decreases. These changes provide evidence that condensation reactions take place in the coal tar pitch. These reactions proceed through the stage of the formation of free radicals obtained as a result of hydrogen rupture from the compounds of coal tar pitch.

So, reactions with nitroaromatic compounds may be used to modify the coal tar pitch. The effect of the addition of nitroaromatic compounds on the rate of coking in coal tar pitch and on the yield of the coke residue was described previously [19, 20]. It was demonstrated in [20] that, along with an increase in the yield of coke, carbonization of a mixture of coal tar pitch with trinitrotoluene suppressed the formation of the mesophase in pitch, and isotropic non-graphitized carbon is formed as a result of cross-linking with the evolution of water even at 200 °C. In patent [21], to

enhance the yield of coke from coal tar pitch, its carbonization with coal tar pitch containing nitro groups after nitration with a nitrating agent is used.

CONCLUSION

It is demonstrated by the example of reactions with model organic compounds that coal tar pitch when used as a solvent is able to exhibit hydrogen-donor properties within temperature range 270–300 °C. Hydrogen transfer from polyaromatic compounds of coal tar pitch, similarly to the reactions of hydrogen transfer from classical hydrogen donors, hydroaromatic compounds, reduced nitrobenzene into aniline and leads to thermal dehalogenation of chlorophenols. Hydrogen transfer from polyaromatic compounds forming the basis of coal tar pitch is accompanied by condensation reactions, which results in the changes of coal tar pitch characteristics.

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