Thermal Stability Study of 4-(1-Adamantyl)phenol

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Abstract—The thermal stability of 4-(1-adamantyl)phenol has been studied in the temperature range of 703–753 K, the components of the thermolysis reaction mixture have been identified, and the rate constants and parameters of the Arrhenius equation for the thermal degradation of the compound under study have been calculated. It has been found that of the thermal stability of 4-(1-adamantyl)phenol significantly surpasses that of 4-*tert*-butylphenol.

Keywords:4-(1-adamantyl)phenol, thermal stability, thermal degradation, isomerization, kinetics, rate constant, Arrhenius equation

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It is known that the modification of organic compounds and polymers with adamantane and its derivatives imparts additional resistance against extreme mechanical impacts to materials and increases their thermo-oxidative stability.

Currently, a great deal of attention is being paid to carboxylic acid esters of the adamantane series as promising components of thermally stable lubricating oils. Thus, Bagrii and Maravin [1] evaluated the viscosity-temperature properties and thermo-oxidative stability of alkyl esters of 5,7-dimethyladamantane-1,3-dicarboxylic acids and showed their advantages over conventional lubricating oils. The cited authors have recommended using such structures as thermally stable synthetic lubricating oils for gas turbine power plants and as cable oil in view of strong electrical insulation properties. The results of extensive studies [2-5]on the physicochemical characteristics and thermooxidative stability of esters of dicarboxylic acids of the adamantane series also show serious advantages of this type of compounds in the development of unique lubricating materials.

Adamantane derivatives are also of great interest in the creation of advanced polymers. For example, it has been shown in [6, 7] that epoxy resins based on 1,3bis(4-hydroxyphenyl)adamantane are characterized by increased hardness and thermal stability and have improved dielectric properties. According to the data of the patent [8], copolymers of dialkyladamantane and di-*tert*-butylbenzenes possess a high glass transition point (182°C), are resistant to extreme temperatures and thermo-oxidative degradation and find application as protective coatings. The results of the studies devoted to adamantylphenols show the possibility of their effective application as inhibitors and antioxidants. Sokolenko et al. [9] have shown that 4-(1-adamantyl)phenol and 2,4-di-(1-adamantyl)phenol exhibit high antioxidant activity by way of example of the model reaction of cumene oxidation. The prospects for application of adamantyl-substituted phenols, cresols, catechol, and hydroquinone as radical chain polymerization inhibitors in the processing of liquid pyrolysis products are discussed in [10, 11].

Overall, taking into account the above information, the question about the thermal stability of adamantane derivatives including adamantylarenes plays a serious role in the development of advanced polymer materials and lubricants.

EXPERIMENTAL

Initial Substances

4-(1-Adamantyl)phenol (4-(1-Ad)Ph) was synthesized by alkylating phenol (provided by Novokuibyshevsk Petrochemical Company, 99.9 wt % by gasliquid chromatography (GLC)) with 1-bromoadamantane at 353 K in a jacketed glass reactor equipped with a stirrer and a reflux condenser. The thermostating was provided by benzene boiling in the reactor jacket.

To a phenol melt, Amberlyst 36 Dry sulfonated cation-exchange resin preliminarily dried to a constant weight at 105° C in an air bath was added in amount of 30 wt % and held for 30 min under constant stirring for the catalyst to swell. Then, 1-bromoadamantane was added and stirring was continued for another 30 min. The phenol/1-bromoadamantane molar ratio was in the range of (4-3)/1.

The catalyst was separated from the reaction mixture by vacuum filtration and rinsed with hot acetonitrile on the filter; the resulting solution was combined with the reaction products. The solvent was distilled off under atmospheric pressure, and the excess of phenol, under vacuum. The residue was recrystallized from acetonitrile; the white needle-like crystals formed were filtered off and dried at room temperature. The concentration of 4-(1-Ad)Ph was 99.9 wt % by GLC after the removal of the solvent.

Procedure for Studying 4-(1-Ad)Ph Thermolysis

The thermal stability of 4-(1-Ad)Ph in the gas phase was studied in a the temperature range of 703– 753 K (in increments of 5 K) by thermostating in enclosed reactors-glass capillaries sealed on both sides. The substances were preliminarily dehydrated. and the capillary was purged with helium after loading. The schematic of the oven in which the samples were thermostated is presented in our paper [12] describing the investigation of the thermal stability of 4-tertbutylphenol (4-TBPh). The accuracy of temperature control in the isothermal zone was provided within $\pm 1^{\circ}$ C. The time to reach isothermal conditions after placing the capillary into the oven did not exceed 60 s. The pyrolysis process was completed by quenching in a cooled test tube, after which the capillary was slightly notched by a needle-point file, immersed into a test tube with a solvent, and broken with a stainless steel rod. Ethanol was used as the solvent.

The kinetics of 4-(1-Ad)Ph thermolysis was studied at the conversion value within 30%. In this case, the number of moles increased by no more than 5% of the initial value during the process, because of which an assumption was adopted about the possibility of the transition from the number of moles of the products to molar concentration when evaluating the changes in the thermolyzate composition.

Product Analysis and Identification

GLC was used as the main method of analysis of the reaction mixtures. The analysis was performed on a Kristall 2000M instrument equipped with a flame ionization detector, a carrier gas flow splitter, and a quartz capillary column ($60 \text{ m} \times 250 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m}$) with the bonded stationary phase SE-30. Helium used as the carrier gas had the column inlet pressure of 3 atm. The evaporator temperature was 250°C, and the detector temperature was 280°C.

The quantitative analysis of the composition of the reaction mixture was performed using the internal standard method with $n-C_{24}H_{50}$ (99.9 wt % by GLC);

The qualitative analysis of the components of the mixtures was performed by GC/MS on an Agilent 6850 gas chromatograph equipped with an Agilent 19091S-433E capillary column (30 m \times 250 µm \times 0.25 µm) with an HP-5MS stationary phase and an Agilent 5975CVL MSD mass selective detector at an ionizing potential of 70 eV.

4-(1-Adamantyl)phenol Thermolysis Reaction Mixture

A typical chromatogram of the 4-(1-Ad)Ph thermolysis products is given in Fig. 1:

The products were identified by GC/MS using the spectral data (EI, 70 eV) from the NIST 2017 library [13].

4-MePh, 4-EtPh, 4-IPPh, and 4-NPPh were additionally identified by comparing the retention times of the components of the reaction mixture under study with the reference standards of the compounds. It was found as a result that the position isomers of the specified alkylphenols (APhs) were absent in the 4-(1-Ad)Ph thermolyzate.

To identify the structure of components 14, 16, 17, 19, and 21-24, we used the data, rules, and approaches described in [14–19], finding the correlations between the degradation of adamantylarenes in the mass spectrometer chamber under electron ionization and thermal decomposition. The correctness of this approach is confirmed in the works by Lobodin and Lebedev [20] and Dougherty [21]. The assumption about the structure of components A_1 and A_2 (17, 22) was additionally based on the data of the study of the thermal stability and degradation of 1,3-dimethyladamantane [22], in which similar adamantane cage opening products due to breaking of one or two bonds between the bridgehead and bridge carbons were found. The characteristics of the mass spectra of components 12-24 are presented in Table1, and their structures are shown in Fig. 1.

RESULTS AND DISCUSSION

Analysis of Thermal Transformations of 4-(1-Ad)Ph

The composition of the main products of thermolysis of 4-(1-Ad)Ph at the process temperature of 733 K selected from the middle of the range under study of 703–753 K is shown in Table 2. All the features revealed for this temperature point are characteristic for the entire temperature range examined.

The information about the character of change in the concentrations of all the individual products and groups of components in the reaction mixture is reflected in Fig. 2.

The analysis of the possible interconversion of the identified components was based on the existing information about the pathways and products of degrada-



Fig. 1. Chromatogram of the reaction mixture of 4-(1-Ad)Ph thermolysis (733 K, 17 min): (1) toluene; (2) o-, m-, and p-xylenes; (3) trimethylbenzene (TMB); (4) phenol; (5) adamantane; (6) 4-MePh; (7) isobutenylbenzene (IBenB); (8) 1-methylindane (1-MeIn); (9) 4-ethylphenol (4-EtPh); (10) 4-isopropylphenol (4-IPPh); (11) 4-n-propylphenol (4-NPPh); (12) 4-hydroxybiphenyl (4-HBPh); (13) (1-adamantyl)benzene (1-(Ad)B); (14) 4-hydroxy-3'-methyl-biphenyl (4-H-3'-MeBPh); (15) 1-benzyl(adamantane) (1-BAd); (16) 4-(1-adamantyl)toluene (4-(1-Ad)T); (17) component A₁; (18) unidentified (X₁); (19) 2-(1-adamantyl)phenol (2-(1-Ad)Ph); (20) 4-(1-Ad)Ph; (21) 4-(2-adamantyl)phenol (4-(2-Ad)Ph); (22) component A₂; (23) 4-(1-adamantyl)-2-methylphenol (4-(1-Ad)-2-MePh); and (24) 4-(1-adamantyl)-2,6-dimethylphenol (4-(1-Ad)-2,6-di-MePh).

tion of adamantane derivatives by thermolysis and electron ionization [14–16, 19, 22]; the character of the rate curves (Fig. 2) according to the data by S. Walas [23] for typical complex reactions was also taken into account.

Thus, 2-(1-Ad)Ph, 4-(2-Ad)Ph, and components A_1 and A_2 were attributed to the products of direct transformation of 4-(1-Ad)Ph (Fig. 2).The initial stage of thermolysis of 4-(1-Ad)Ph was characterized by a high rate of 2-(1-Ad)Ph and 4-(2-Ad)Ph buildup throughout the entire range of the temperatures. For example, the concentrations of 2-(1-Ad)Ph and 4-(2-

Ad)Ph were 0.42 and 0.18 mol %, respectively, at 733 K over the first minute at a 4-(1-Ad)Ph conversion of 0.85 mol % (Table 2). Taking into account only the positional changes of the substituents in the structure, these components were defined as isomerization products. This assumption is based on the substantial effect of isomerization processes found in our studies on the thermolysis of 4-*tert*-butylphenol [12] and 4-*tert*-butyldiphenyl oxide [24]; thus, the mechanism of 4-(1-Ad)Ph \rightarrow 4-(2-Ad)Ph isomerization can be similar, involving a three-membered intermediate cycle:



Apparently, the formation of components A_1 and A_2 results from 4-(1-Ad)Ph degradation via the

 C_{bridge} - $C_{bridgehead}$ bond rupture. Presumably, the process proceeds by the following mechanism:

 Table 1. Characteristic of the mass spectra of 4-(1-Ad)Ph and products of its thermolysis

| Species | Mass spectrum, 70 eV: m/z , major abundances (rel. %) |
|---------|--|
| 12 | M ⁺ *, 170(100); 165(2), 157(2), 152(4), 141(20), 128(1), 115(12), 107(0.2) |
| 13 | M ⁺ , 212(100); 169(13),155(100), 141(5), 128(7), 115(8), 103(2), 94(8), 91(9) |
| 14 | M^{+} , 184(100); 167(5), 165(12), 157(1), 155(5), 153(6), 141(4), 128(4), 121(0.2) 115(4), 107(0.3), 91(2) |
| 15 | M ⁺ , 226(50); 207(5), 183(10), 169(10), 153(2), 135(100), 128(1), 115(5), 107(11), 93(12), 91(9), 79(8) |
| 16 | M^{+} , 226(76); 211(2), 194(1), 183(7), 169(100), 154(11), 141(5), 132(15), 128(6), 115(5), 105(7), 94(3), 91(6) |
| 17 | M ⁺ , 228(28); 213(4), 198(3), 185(100), 172(17), 157(7), 152(2), 144(2), 141(2), 131(1), 128(2), 115(2), 107(5), 94(1), 91(2) |
| 18 | M ⁺ , 226(100); 211(9), 197(6), 183(46), 170(30), 165(8), 157(6) 153(7), 144(4), 141(6), 128(6), 115(7), 103(1), 94(1), 91(1) |
| 19 | M ⁺ , 228(100); 213(2), 200(1), 185(20), 171(88), 165(4), 158(6), 153(23), 145(6), 141(3), 134(14), 131(7), 128(7), 121(5), 115(7), 107(14), 94(7), 91(8) |
| 20 | M ⁺ , 228(80); 213(1), 200(1), 199(1), 185(11), 171(100), 165(1), 157(5), 153(21), 145(4), 141(3), 134(23), 131(4), 128(5), 119(3), 115(5), 107(11), 94(2), 91(6) |
| 21 | M ⁺ , 228(100); 211(6), 200(1), 199(1), 185(3), 171(1), 165(1), 157(1), 152(1), 145(3), 141(1), 133(5), 131(3), 121(6), 115(3), 107(24), 93(6), 91(5) |
| 22 | M ^{+*} , 228(61); 213(2), 208(7), 195(1), 181(1), 169(3), 157(6), 152(1), 146(14), 135(12), 131(11), 127(10), 120(100), 107(23), 92(22), 91(6) |
| 23 | M ⁺ , 242(100); 224(2), 213(1), 209(1), 199(12), 185(98), 171(6) 167(13), 157(3), 152(5), 148(22), 141(3), 131(2), 128(3), 121(7), 115(3), 91(3) |
| 24 | M ⁺ , 256(100); 241(3), 213(10), 209(1), 199(75), 183(4), 171(25) 162(21), 157(2), 153(7), 147(5), 141(3), 135(8), 128(4), 121(1), 115(4), 107(1), 91(6) |
| | |



The composition of the reaction mixture (Table 2) shows that in the process developing within the 4-(1-Ad)Ph conversion of 10%), the degradation of the adamantyl substituent form components A_1 and A_2 is not inferior to the decomposition by the $C_{Ar}-C_{Ad}$

bond with the formation of phenol and adamantane. The isomerization of 4-(1-Ad)Ph with the formation of 2-(1-Ad)Ph and 4-(2-Ad)Ph has a predominant character within the specified limits of conversions.

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|--------------|--------|------------|------------|--------|------------------|----------------|------------|------------|------------|----------------|
| Time, min | Phenol | Adamantane | $\sum APh$ | 4-HBPh | 4-H-3'- MeBPh | A ₁ | 2-(1-Ad)Ph | 4-(1-Ad)Ph | 4-(2-Ad)Ph | A ₂ |
| 0.0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 100.00 | 0.00 | 0.00 |
| 1.0 | 0.11 | 0.01 | 0.00 | 0.00 | 0.00 | 0.04 | 0.42 | 99.15 | 0.18 | 0.04 |
| 1.5 | 0.10 | 0.01 | 0.00 | 0.00 | 0.00 | 0.08 | 0.57 | 98.95 | 0.19 | 0.06 |
| 2.0 | 0.23 | 0.03 | 0.02 | 0.00 | 0.00 | 0.22 | 0.69 | 98.30 | 0.37 | 0.07 |
| 3.0 | 0.60 | 0.14 | 0.02 | 0.00 | 0.00 | 0.58 | 0.94 | 97.23 | 0.21 | 0.13 |
| 5.0 | 0.73 | 0.22 | 0.04 | 0.01 | 0.01 | 0.64 | 1.23 | 96.32 | 0.40 | 0.12 |
| 6.0 | 1.02 | 0.37 | 0.10 | 0.01 | 0.03 | 0.91 | 1.30 | 94.98 | 0.65 | 0.14 |
| 6.5 | 0.82 | 0.23 | 0.09 | 0.02 | 0.02 | 1.14 | 1.46 | 95.11 | 0.58 | 0.15 |
| 7.0 | 0.76 | 0.25 | 0.19 | 0.03 | 0.06 | 1.23 | 1.46 | 93.96 | 0.98 | 0.13 |
| 8.0 | 1.16 | 0.44 | 0.11 | 0.01 | 0.02 | 1.29 | 1.52 | 93.95 | 0.58 | 0.14 |
| 9.0 | 1.53 | 0.69 | 0.15 | 0.04 | 0.09 | 1.67 | 1.37 | 92.60 | 0.89 | 0.16 |
| 10.0 | 1.72 | 0.61 | 0.15 | 0.02 | 0.11 | 1.51 | 1.33 | 92.47 | 0.78 | 0.10 |
| 11.0 | 1.28 | 0.54 | 0.31 | 0.05 | 0.15 | 2.02 | 1.39 | 91.47 | 1.26 | 0.13 |
| 12.0 | 1.90 | 0.79 | 0.32 | 0.06 | 0.19 | 2.25 | 1.39 | 89.91 | 1.36 | 0.11 |
| 14.0 | 2.89 | 1.32 | 0.30 | 0.06 | 0.15 | 1.90 | 1.30 | 88.68 | 1.41 | 0.10 |
| 15.0 | 3.01 | 1.65 | 0.43 | 0.05 | 0.32 | 2.10 | 1.24 | 87.19 | 1.55 | 0.10 |
| 17.0 | 3.58 | 1.91 | 0.53 | 0.09 | 0.42 | 2.41 | 1.01 | 85.13 | 1.96 | 0.09 |
| 20.0 | 4.31 | 2.35 | 0.79 | 0.09 | 0.62 | 2.91 | 0.90 | 82.40 | 1.94 | 0.09 |
| 23.0 | 4.67 | 2.72 | 1.22 | 0.15 | 0.77 | 3.24 | 0.61 | 79.51 | 2.10 | 0.07 |
| 25.0 | 5.71 | 3.24 | 1.32 | 0.16 | 0.72 | 3.33 | 0.56 | 77.01 | 2.09 | 0.08 |
| 27.0 | 5.81 | 3.36 | 1.81 | 0.21 | 0.85 | 3.44 | 0.43 | 75.05 | 2.28 | 0.08 |

Table 2. Main products of 4-(1-Ad)Ph thermolysis at 733 K, mol %

4-MePh, 4-EtPh, 4-IPPh, and 4-NPPhare presented as a group of total alkylphenols (\sum APh). The thermolysis products of 4-(1-Ad)Ph which reached noticeable concentrations only in the developed process at a 4-(1-Ad)Ph conversion over 10%, such as toluene, xylenes, TMB, IBenB, 1-MeIn, X_I, (1-Ad)B, 1-BAd, 4-(1-Ad)T, 4-(1-Ad)-2-MePh, and 4-(1-Ad)-2,6-di-MePh, are not presented in Table 2.

With an increase in the depth of 4-(1-Ad)Ph transformation, the rate of formation of phenol and adamantane increases, which is explained by the growth in the intensity of the degradation processes in general and by the degradation of 2-(1-Ad)Ph and 4-(2-Ad)Ph in particular. This is also confirmed by the data on the composition of the reaction mixture (Table 2) and the shape of the rate curves of these components.

As regards the breaking of the $C_{Ar}-C_{Ad}$ bond throughout the entire study range, we found that the concentration of adamantane was substantially lower than the concentration of phenol in the developing process. With an increase in the degree of conversion of 4-(1-Ad)Ph and in the thermolysis temperature, the *C*(adamantane)/*C*(phenol) molar ratio increases but does not reach 1.0 mol/mol. Thus, it is stabilized at the levels of 0.35–0.40 at 703 K, 0.55–0.60 at 733 K, and 0.65–0.75 at 753 K (Fig. 3).

Such a character of the process probably indicates the destruction of the adamantyl radical formed as a result of hydrolytic breaking of the $C_{Ar}-C_{Ad}$ bond in 4-(1-Ad)Ph. According to E.I. Bagrii [14], the stability of the adamantyl radical is even lower than that of the *tert*-butyl radical in some cases. Apparently, the adamantyl radical formed upon the breaking of the C_{Ar} - C_{Ad} bond during the thermolysis of 4-(1-Ad)Ph undergo degradation with the formation of hydrogen, light C_1 - C_4 hydrocarbons, and alkylaromatic hydrocarbons similarly to the degradation of adamantane and methyl- and dimethyladamantanes [14, 22]. As is seen from the data presented in Fig. 3, the concentration of adamantane relative to phenol increases with an increase in the depth of the process, which apparently results from the appearance of molecular and atomic hydrogen, which promote the stabilization of the adamantyl radical and its conversion to adamantane.

To verify this hypothesis, we compared the character of the thermolysis of 4-(1-Ad)Ph at 703 K in helium and hydrogen atmospheres (Fig. 3). The size of the capillaries and degree of loading of the substance remained unchanged, but the capillary was filled with hydrogen instead of helium. As a result, the C(adamantane)/C(phenol) ratio increased at each time point and reached a level of 0.7 mol/mol in the limit, with the level of the concentration of phenol remain-



Fig. 2. Concentration curves of the products of thermal transformations of 4-(1-Ad)Ph at 733 K: (1) 4-(1-Ad)Ph, (2) 2-(1-Ad)Ph, (3) phenol, (4) adamantane, (5) component A_1 , (6) 4-(2-Ad)Ph, (7) 4-(1-Ad)-2-MePh, (8) 4-(1-Ad)-2,6-di-MePh, (9) 4-MePh, (10) 4-EtPh, (11) 4-IPPh, (12) 4-NPPh, (13) (1-Ad)B, (14) Σ (1-BAd, 4-(1-Ad)T), (15) X_1 , (16) component A_2 , (17) 4-HBPh, (18) 4-H-3'-MeBPh, and (19) Σ (toluene, xylenes, TMB, IBenB, 1-MeIn).

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Fig. 3. Change in the *C*(adamantane)/*C*(phenol) molar concentration ratio: (1) 703 K (He), the ultimate conversion of 4-(1-Ad)Ph is 7.95%; (2) 703 K (H₂), the ultimate conversion of 4-(1-Ad)Ph is 10.33%; (3) 733 K (He), the ultimate conversion of 4-(1-Ad)Ph is 24.95%; and (4) 753 K (He), the ultimate conversion of 4-(1-Ad)Ph is 26.38%.



Fig. 4. Change in the concentration of the products of 4-(1-Ad)Ph thermolysis in helium and hydrogen atmospheres at 703 K: (1) 4-(1-Ad)Ph (He), (2) 4-(1-Ad)Ph (H₂), (3) 2-(1-Ad)Ph (He), (4) 2-(1-Ad)Ph (H₂), (5) adamantane (He), (6) phenol (He), (7) adamantane (H₂), and (8) phenol (H₂).

ing unchanged and that of adamantane increasing (Fig. 4).

In general, the intensity of the degradation processes increased in the hydrogen atmosphere. The rate constant of the 4-(1-Ad)Ph \rightarrow products decomposition increased by a factor of 1.78; thus, $k_{703} = (3.21 \pm 0.07) \times 10^{-5} \text{ s}^{-1}$ in an inert atmosphere and $k_{703(\text{H}_2)} = (5.71 \pm 0.36) \times 10^{-5} \text{ s}^{-1}$ in a hydrogen atmosphere. The fact that the character of 2-(1-Ad)Ph buildup slightly changed also generated interest.

Regarding the formation routes of other products of 4-(1-Ad)Ph thermolysis in the inert atmosphere in the range of 703–753 K, we made the following assumptions:

(1) 4-(1-Ad)-2-MePh and 4-(1-Ad)-2,6-di-MePh are the products of successive methylation of 4-(1-Ad)Ph;

(2) Toluene, xylenes, TMB, IBenB, and 1-MeIn are the products of adamantane degradation;

(3) 4-HBPh and 4-H-3'-MeBPh are the degradation products of component A_1 ;

(4) 1-AdBis is the product of degradation of 4-(1-Ad)Ph as a result of abstraction of hydroxyl;

(5) Alkylphenols—4-MePh, 4-EtPh, and 4-IPPh—are the products of degradation of component A_2 , and 4-NPPh is the product of isomerization of 4-IPPh;

(6) 1-BAd and 4-(1-Ad)T probably result from the recombination of adamantyl and benzyl radicals.

Transformation routes similar to those presented in clauses 1-3 were revealed upon the thermolysis of 1,3-dimethyladamantane [22]. The existence of route 4 was shown in the study of hydroquinone thermolysis in the range of 623-1123 K [24].

Calculation of the Arrhenius Parameters for the Reaction $4-(1-Ad)Ph \rightarrow Products$

The kinetic analysis of the experimental data for the 4-(1-Ad)Ph \rightarrow products thermal decomposition

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 Table 3. Values for the rate constants of thermal decomposition of 4-(1-Ad)Ph

| τV | $4-(1-Ad)Ph \rightarrow products$ | | | | | | | |
|------|-------------------------------------|----|-----------------------|------------------------|--|--|--|--|
| 1, к | $k_i \times 10^5, \mathrm{s}^{-1}$ | n | <i>R</i> ² | ultimate conversion, % | | | | |
| 703 | 3.21 ± 0.07 | 33 | 0.99 | 7.95 | | | | |
| 708 | 4.12 ± 0.28 | 24 | 0.94 | 10.08 | | | | |
| 713 | 6.88 ± 0.33 | 22 | 0.97 | 15.04 | | | | |
| 718 | 9.08 ± 0.54 | 20 | 0.96 | 13.70 | | | | |
| 723 | 10.9 ± 0.5 | 21 | 0.98 | 24.63 | | | | |
| 728 | 13.8 ± 0.5 | 18 | 0.99 | 21.58 | | | | |
| 733 | 17.4 ± 0.5 | 21 | 0.99 | 24.95 | | | | |
| 738 | 20.1 ± 0.8 | 18 | 0.98 | 15.90 | | | | |
| 743 | 25.6 ± 1.5 | 18 | 0.96 | 14.20 | | | | |
| 748 | 49.1 ± 2.3 | 15 | 0.98 | 22.46 | | | | |
| 753 | 60.8 ± 15.6 | 17 | 0.93 | 26.38 | | | | |

reaction was performed at each temperature point in the range of 703-753K and the entire range of 4-(1-Ad)Ph conversions using the equation for the of the first-order rate constant (1):

$$\ln \frac{C_0}{C} = k\tau. \tag{1}$$

The values of the calculated reaction rate constants are presented in Table 3.

The parameters were calculated from the experimental values of the rate constants by linearization of the Arrhenius equation in the $\ln k_i - 1000/T$ coordinates. It has been found as a result that the preexponential factor is $k_0 = 10^{13.7 \pm 0.8}$ and the activation energy is $E_a = 244.8 \pm 11.7$ kJ/mol for the 4-(1-Ad)Ph \rightarrow products decomposition reaction in the studied range of temperatures.

For comparison, in the temperature range of 673– 738 K, the activation energy is lower by 14.9 kJ/mol $(E_a = 229.9 \pm 4.1 \text{ kJ/mol})$ at a comparable value of the preexponential factor $(k_0 = 10^{13.2 \pm 0.3})$ for the 4-TBPh \rightarrow products degradation process [12].

The evaluation of the rate constants presented in Table 3 as the most sensitive characteristics also shows that 4-(1-Ad)Ph is more stable and is capable of retaining its structure at higher temperatures than 4-TBPh. The comparative analysis of the degradation rate constants of 4-(1-Ad)Ph and 4-TBPh in the temperature range of 703–738 K showed that the degradation of 4-(1-Ad)Ph proceeds three- to fourfold slower on the average.

CONCLUSIONS

It has been found as a result of the study that the thermolysis of 4-(1-adamantyl)phenol proceeds via three routes in the range of 703–753 K, namely, isom-

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erization with the formation of 4-(2-adamantyl)phenol and 2-(1-adamantyl)phenol, dissociation of the $C_{bridgehead}-C_{bridge}$ bonds in the adamantyl substituent, and degradation via $C_{Ar}-C_{Ad}$ bond rupture leading to the formation of phenol and products of decomposition of the adamantyl substituent. The processes of isomerization and dissociation of the $C_{bridgehead}-C_{bridge}$ bonds with the cleavage of the adamantane cycle make a significant contribution to the thermal degradation of 4-(1-adamantyl)phenol.

The mechanism of $4-(1-Ad)Ph \rightarrow 4-(2-Ad)Ph$ radical isomerization through a three-membered intermediate cycle has been proposed.

The preexponential factor of $k_0 = 10^{13.7\pm0.8}$ and the activation energy of $E_a = 244.8 \pm 11.7$ kJ/mol found for the 4-(1-Ad)Ph \rightarrow products decomposition reaction in the temperature range of 703–753 K show that the thermal stability of 4-(1-Ad)Ph significantly surpass that of 4-TBPh.

The information acquired as a result of this study is aimed at expanding the theoretical and informational background for the development of thermally stable composite and lubricating materials, high-temperature stabilizers and antioxidants, and monomers for the polymers with improved properties.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

SUPPLEMENTARY MATERIALS

Supplementary materials are available for this article at doi: 10.1134/S0965544120110171 and are accessible for authorized users.

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