# Thermal Stability Study of 4-tert-Butylphenol

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**Abstract**—The thermal stability of 4-*tert*-butylphenol has been studied in the temperature range of 673—738 K, the components of the thermolysis reaction mixture have been identified, a kinetic model of the process has been proposed, and the rate constants and parameters of the Arrhenius equation have been calculated for all of the reactions considered. The predominant role of 4-*tert*-butylphenol isomerization transformations has been established. Information on the 4-*tert*-butylphenol thermal stability facilitates to a more substantiated approach to its use as an additive that increases the oxidative stability of fuels and lubricants, as well as an antioxidant for polymer compositions.

**Keywords:** 4-*tert*-butylphenol, thermolysis, thermal stability, thermal degradation, isomerization, kinetics, rate constant, Arrhenius parameters

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Alkylphenols (**AP**s) are of great practical importance in the development of modern industry. They are used in the manufacture of plastic foams, polymer emulsions, surfactants, additives for oils and fuels, and stabilizers of thermal destruction of polymers. Aminoalkylphenols are used in the preparation of fuel emulsions for engines [1-4]. Phenolic resins are used in the production of electrolytic cells and refractory materials [5]. Phenolic antioxidants have a wide range of applications. Nevertheless, the issue of the thermal stability of phenols and their derivatives has been given attention in quite a limited amount of research:

• Kachatryan et al. [6, 7] obtained data on the kinetics of phenoxyl ( $C_6H_5O^{\cdot}$ ) and cyclopentadienyl ( $C_5H_5^{\cdot}$ ) radicals formation during the gas-phase phenol pyrolysis at 673–1273 K and reduced pressures.

• Ledesma et al. [8] investigated pyrocatechol pyrolysis under nitrogen atmosphere (at 773-1273 K and contact time of 0.4 s) in order to obtain the kinetic parameters for the formation of condensed polycyclic aromatic hydrocarbons (HCs), which are solid fuels.

• Adounkpe et al. [9] investigated thermal stability of hydroquinone in the gas phase over the temperature range of 623-1123 K; the presence of *p*-quinol and cyclopentadienyl radicals was established, and the effect of the process temperature on their concentration was revealed.

• In [10], Hamama and Navar described the thermal decomposition of 2-*tert*-butyl-4-methoxyphenol, *n*-propylgallate, 2-*tert*-butylhydroquinone and 2,6di-*tert*-butyl-4-methylphenol in air at 458 K. Possible mechanisms for the decomposition of 2-*tert*-butyl-4methoxyphenol, 2,6-di-*tert*-butyl-4-methylphenol and 2-*tert*-butylhydroquinone were proposed. For 2-*tert*-butylhydroquinone, it was established that along with the degradation, the isomerization of the *tert*-butyl substituent to the isobutyl one id possible. However, the results of the cited work are limited to one temperature and do not consider the kinetic parameters of the occurring transformations.

• Sato et al. [11] established the fact of isomerization of the alkyl substituent during pyrolysis of isopropylphenols in supercritical water at 720-820 K; a model of the occurring transformations was proposed, and the reaction rate constants were calculated.

• Repkin [12] investigated the thermal stability of 4-*tert*-butylphenol (4-TBP) in the temperature range of 683–733 K; a model of the decomposition was proposed. However, our studies have shown that the information on the composition of the reaction mixtures of 4-TBP decomposition given in [12] needs to be clarified and the kinetic model should be changed and complemented.

In this study, we considered in more detail the issue of the 4-TBP thermolysis mixture composition and calculated the kinetic parameters for all transformations included in the kinetic model.



Fig. 1. Layout of the experimental setup: (1) oven, (2) reactor filled with quartz sand, (3) one-channel TPM1 temperature monitor-regulator, (4) quartz test tube, (5) quartz guide, (6) laboratory transformer, (7) platinum-rhodium/platinum type S thermocouple, (8) a capillary with the test substance, and (9) isothermal zone.

## **EXPERIMENTAL**

### Starting Materials

4-TBP was synthesized, isolated and purified by us in accordance with the recommendations of [13]. The concentration of the basic substance was 99.9 wt %. 4-TBP was obtained by alkylation of phenol with isobutylene at a temperature of 353 K and an isobutylene : phenol molar ratio of 0.25 in the presence of macroporous Amberlyst 36 Dry sulfonated cation-exchange resin, dried to constant weight; the catalyst charge was 10 wt % relative to the weight of the reaction mixture; contact time, 30 min. The synthesis was carried out in a three-necked flask equipped with a capillary for isobutylene supply, a thermometer, and a reflux condenser with an internal guide for a glass stirrer. Isobutylene flow rate (concentration 99.99%) was adjusted using a calibrated rheometer.

The isolation of 4-TBP was carried out using vacuum rectification ( $p_{res} = 0.8-1.0$  kPa) on laboratory columns with an efficiency of 30 theoretical plates. The purity of the isolated 4-TBP was 99.9 wt %.

The identification of 4-TBP was performed using gas chromatography-mass spectrometry (GC-MS) and a comparison of the spectra and the elution time of the obtained sample with a standard 4-TBP sample (purity 99 wt %) produced by Sigma-Aldrich. The probability of coincidence with the NIST 2011 library data was 99%.

## Procedure for 4-TBP Thermolysis.

The thermolysis was carried out in the gas phase in quartz capillaries ( $l = 20-25 \text{ mm}; d_n = 1.05-$ 1.56 mm), into which the test substance was placed, after which the capillary was purged with helium (purity 99.999%) and sealed with a hydrogen gas burner. The degree of filling with the substance was 20-30 vol %, which corresponded to the weight of the substance of 0.4–0.5 mg. The weighing was carried out on a Shimadzu AUW 120D analytical balance with an accuracy of  $10^{-4}$  g. The thermostating was carried out on a special setup (Fig. 1) ensuring that the temperature in the isothermal zone is maintained constant accurate to within  $\pm 1$  K. The pyrolysis process was always terminated by quenching, which consisted in immediate transferring the capillary from the furnace to a test tube cooled to  $-15^{\circ}$ C. To solve the problem of building the kinetic model of the 4-TBP thermal decomposition, a certain temperature range of the study was chosen: 718 K (interval 673-738 K with a step of 5 K).

## Product Analysis and Identification

The main method for analyzing reaction mixtures was GLC. The analysis was performed on a Kristall 2000 M instrument with the Chromatec Analytic software and hardware system equipped with a flame ionization detector, a precolumn flow splitter, and a quartz capillary column ( $60 \text{ m} \times 250 \mu \text{m} \times 0.25 \mu \text{m}$ ) with an SE-30 bonded stationary phase. Helium was used as a carrier gas; its pressure at the column inlet was 3 atm, the stability of the pressure was ensured by double reduction. The temperature profiles of the column are shown in the corresponding chromatograms (with an error of  $\pm 0.1^{\circ}$ C). The evaporator and detector temperatures were 200 and 280°C, respectively.

In quantitative analysis, *n*-tetradecane was used as an internal standard (purity 99.9 wt % by GLC).

Identification of the components of the mixtures also included GC–MS analysis performed on an Agilent 19091S-433E capillary column (30 m × 250  $\mu$ m × 0.25  $\mu$ m) with an HP-5MS stationary phase (5% diphenylpolysiloxane + 95% dimethylpolysiloxane) and an Agilent 5975C VL MSD mass selective detector at an ionizing energy of 70 eV.

## 4-tert-Butylphenol Thermolysis Reaction Mixture

A typical chromatogram of the pyrolysis products is depicted in Fig. 2.

The main products were identified using the NIST 2011 database to interpret the mass spectra measured for the compounds: phenol (m/z 94), 2-methylphenol (2-MeP) and 4-methylphenol (4-MeP) (m/z 108, m/z 107), 4-ethylphenol (4-EP) (m/z 122, m/z 107), 2-isopropylphenol (2-IPP) and 4-isopropylphenol



**Fig. 2.** Chromatogram of the products of 4-TBP thermal transformations (T = 718 K,  $t_{contact} = 20$  min): (A) phenol, (B) 2-methylphenol (2-MeP), (C) 4-methylphenol (4-MeP), (D) 4-ethylphenol (4-EP), (E) 2-isopropylphenol (2-IPP), (F) 2-*n*-propylphenol (2-NPP), (G) 4-isopropylphenol (4-IPP), (H) 4-*n*-propylphenol (4-NPP), (I) 2-isobutylphenol (2-IBP), (J) 4-TBP, (K) 4-isobutylphenol (4-IBP), (L) 4-*n*-butylphenol (4-NBP) added to the analyzed mixture in order to establish the structure of 4-IBP using the GC–MS method.

(4-IPP)  $(m/z \ 136, m/z \ 121, m/z \ 91, m/z \ 77)$ , 2-*n*-propylphenol (2-NPP) and 4-*n*-propylphenol (4-NPP)  $(m/z \ 136, m/z \ 107, m/z \ 77)$ , and 4-TBP  $(m/z \ 150, m/z \ 155, m/z \ 107)$ .

The coincidence of the mass spectra with those in the NIST 2011 database for all components of the reaction mixture shown in the chromatogram (Fig. 2) was 99%. The structure of 4-MeP, 4-EP, 4-IPP, and 4-NPP was additionally determined by comparing the elution times and spectra of the reaction products with standard Sigma-Aldrich samples with a purity of 99, 99, 98, and 99%, respectively.

4-Isobutylphenol (m/z 150, m/z 107) was identified by comparing the elution times and mass spectra of the component (K) formed upon the thermal transformations of 4-TBP and 4-*n*-butylphenol (4-NBP, component (L)) (> 98% by GLC), which was added to the analyzed mixture. Components K and L had different elution times.

# **RESULTS AND DISCUSSION**

Instead of the expected  $\beta$ -C–C bond cleavage or 4-TBP dealkylation, the thermal treatment primarily resulted in the structural isomerization of the alkyl substituent to form 4-IBP (Fig. 3a). For 30 min of the experiment, its content in the reaction mixture reached 22.70 mol % (at the 4-TBP conversion of 40.80%). In this case, the dealkylation of 4-TBP resulted in the formation of phenol, the concentration of which reached 8.13 mol % within 30 min (Fig. 3d). An analysis of the patterns of the rate curves led to the conclusion that this is the only kind of transformation suffered by the reactant 4-TBP. The source for the formation of the other components of the reaction mixture is 4-IBP. The products of decomposition and further sequential transformations of 4-IBP had significantly lower concentrations. On the whole, 4-IPP, 4-NPP (Fig. 3b), and 4-EP (Fig. 3c) made only 3.96 mol % for 30 min, whereas 4-MeP made 6.03 mol % (Fig. 3d).

As the process depth increased (15-27 min), the positional isomerization of substituents on the phenol aromatic rings with the formation of the 2-isomers of IBP, IPP, NPP and MeP was also observed. In this case, the concentration of 2-IBP was lower than that of 4-IBP by  $2.05 \times 10^3 - 1.36 \times 10^4$  times. Concentrations in the other groups of positional isomers were in the following ratios: 4 - IPP/2 - IPP = (10-25)/1, 4 - NPP/2 - NPP = (15-35)/1, and 4 - MeP/2 - MeP = (20-80)/1. The 2-isomers of TBP and EP were not detected.

Taking into account the significant predominance of isomers with a substituent in the 4-position and the possibility of the formation of 2-isomers due to *para*– *ortho* isomerization, we used the notations 4-IBP, 4-IPP, 4-NPP, 4-MeP for the total 4- and 2-isomers.

To establish possible routes of transformation involving the components listed above, a number of assumptions were adopted based on the structural features of the molecules and the nature of the changes in their concentrations. The main routes are 4-TBP isomerization to 4-IBP, the formation of phenol from 4-TBP due to isobutylene cleavage, the formation of 4-IPP from 4-IBP due to a loss of methylene fragment and rearrangement, 4-MeP formation from 4-IBP due to propylene cleavage, 4-IPP isomerization to form 4-NPP, and degradation of 4-NPP to form 4-EP.

Based on the above assumptions, the following outcomes were obtained:



**Fig. 3.** Changes in the concentration of 4-TBP conversion products in the reaction mixture at 718 K: (a) ( $\blacksquare$ ,-) 4-TBP, ( $\diamond$ , -) 4-IBP; (b) ( $\bigcirc$ ,--) 4-IPP, ( $\blacklozenge$ ,--) 4-IPP; (c) ( $\triangle$ ,--) 4-EP; (d) ( $\bigcirc$ ,--) 4-MeP, ( $\diamond$ ,--) Phenol.



Fig. 4. Scheme of transformations occurring during 4-TBP thermolysis (718 K).

• general scheme of transformations in the system (Fig. 4)

• kinetic model of the process:

$$\frac{d[4 - \text{TBP}]}{dt} = -k_1[4 - \text{TBP}] - k_2[4 - \text{TBP}], \quad (1)$$

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$$\frac{d[4 - IBP]}{dt} = k_1[4 - TBP] - k_3[4 - IBP] - k_4[4 - IBP],$$
(2)

$$\frac{d[4 - IPP]}{dt} = k_3[4 - IBP] - k_5[4 - IPP], \quad (3)$$

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Table 1. Rate constants of thermal transformations accompanying 4-TBP degradation in the range of 673–738 K

Reaction	4-TBP	4-TBP	4-IBP	4-IBP	4-IPP	4-NPP
	4-IBP	phenol	4-IPP	4-MeP	4-NPP	4-EP
$\frac{k_i,  \mathrm{s}^{-1}}{T,  \mathrm{K}}$	$k_1$	k <sub>2</sub> ,	<i>k</i> <sub>3</sub>	$k_4$	$k_5$	k <sub>6</sub>
673	$1.90 \times 10^{-5}$	$2.43 \times 10^{-6}$	$3.50 \times 10^{-6}$	$5.57 \times 10^{-6}$	$2.11 \times 10^{-4}$	$3.12 \times 10^{-5}$
678	$2.91 \times 10^{-5}$	$3.69 \times 10^{-6}$	$5.86 \times 10^{-6}$	$9.59 \times 10^{-6}$	$2.92 \times 10^{-4}$	$4.70 \times 10^{-5}$
683	$3.28 \times 10^{-5}$	$5.27 \times 10^{-6}$	$8.64 \times 10^{-6}$	$1.42 \times 10^{-5}$	$3.86 \times 10^{-4}$	$6.59 \times 10^{-5}$
688	$5.04 \times 10^{-5}$	$7.49 \times 10^{-6}$	$1.27 \times 10^{-5}$	$2.10 \times 10^{-5}$	$5.08 \times 10^{-4}$	$9.20 \times 10^{-5}$
693	$7.27 \times 10^{-5}$	$1.06 \times 10^{-5}$	$1.85 \times 10^{-5}$	$3.07 \times 10^{-5}$	$6.65 \times 10^{-4}$	$1.28 \times 10^{-4}$
698	$8.18 \times 10^{-5}$	$1.49 \times 10^{-5}$	$2.68 \times 10^{-5}$	$4.48 \times 10^{-5}$	$8.68 \times 10^{-4}$	$1.77 \times 10^{-4}$
703	$1.10 \times 10^{-4}$	$2.08 \times 10^{-5}$	$3.86 \times 10^{-5}$	$6.49 \times 10^{-5}$	$1.13 \times 10^{-3}$	$2.43 \times 10^{-4}$
708	$1.75 \times 10^{-4}$	$3.35 \times 10^{-5}$	$6.52 \times 10^{-5}$	$1.15 \times 10^{-4}$	$1.61 \times 10^{-3}$	$3.82 \times 10^{-4}$
713	$1.76 \times 10^{-4}$	$4.02 \times 10^{-5}$	$7.91 \times 10^{-5}$	$1.34 \times 10^{-4}$	$1.89 \times 10^{-3}$	$4.55 \times 10^{-4}$
718	$2.35 \times 10^{-4}$	$5.73 \times 10^{-5}$	$1.55 \times 10^{-4}$	$2.37 \times 10^{-4}$	$2.44 \times 10^{-3}$	$6.42 \times 10^{-4}$
723	$3.06 \times 10^{-4}$	$7.61 \times 10^{-5}$	$1.59 \times 10^{-4}$	$2.72 \times 10^{-4}$	$3.11 \times 10^{-3}$	$8.36 \times 10^{-4}$
728	$4.27 \times 10^{-4}$	$1.04 \times 10^{-4}$	$2.24 \times 10^{-4}$	$3.85 \times 10^{-4}$	$3.97 \times 10^{-3}$	$1.13 \times 10^{-3}$
733	$5.70 \times 10^{-4}$	$1.35 \times 10^{-4}$	$2.92 \times 10^{-4}$	$4.75 \times 10^{-4}$	$5.05 \times 10^{-3}$	$1.39 \times 10^{-3}$
738	$6.92 \times 10^{-4}$	$1.80 \times 10^{-4}$	$3.65 \times 10^{-4}$	$6.55 \times 10^{-4}$	$6.05 \times 10^{-3}$	$1.98 \times 10^{-3}$

\* Error in determining the values of the rate constants was no more than 5%.

$$\frac{d[4 - NPP]}{dt} = k_5[4 - IPP] - k_6[4 - NPP].$$
(4)

$$\frac{d[4-\mathrm{EP}]}{dt} = k_6[4-\mathrm{NPP}]. \tag{5}$$

$$\frac{d[4 - \operatorname{MeP}]}{dt} = k_4[4 - \operatorname{IBP}].$$
(6)

The values of the rate constants for individual transformations (Table 1) were determined using a differential method by coprocessing all experimental data with optimization criterion (7) for each temperature:

$$\sum_{n} \left( \left( \frac{dC_i}{dt} \right)_{\text{experiment}} - \left( \frac{dC_i}{dt} \right)_{\text{calculation}} \right)^2 \to \min, \quad (7)$$

where *n* is the number of measurements.

The adequacy of the model is illustrated in Fig. 5, where the experimental concentrations of the components are compared with the calculated ones obtained by the Runge–Kutta method using the rate constants listed in Table 1. The Pearson goodness of fit value for comparing the concentrations was 0.99.

The values of the  $k_1$  and  $k_2$  rate constants presented in Table 1 indicate that upon thermal action on 4-TBP the 4-TBP  $\rightarrow$  4-IBP isomerization proceeds 4 times faster than destructive transformations.

4-IBP undergoes degradation yielding 4-IPP and 4-MeP (reactions 3 and 4). In this case, propylene cleavage resulting in the formation of 4-MeP as a product proceeds 1.5 times faster than the process leading to 4-IPP ( $k_3 = 1.55 \times 10^{-4}$ ,  $k_4 = 2.37 \times 10^{-4}$  for T = 718 K).



Fig. 5. Comparison of experimental ( $\Box$ ) and calculated (-) data on the changes in concentrations of the products of 4-TBP thermal transformations at 718 K.

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**Table 2.** Rate constants for 4-TBP  $\rightarrow$  products thermal transformations occurring during 4-TBP thermolysis at 673–738 K

<i>T</i> , K*	1000/ <i>T</i>	$k_i,  { m s}^{-1}$	$\ln(k_i)$
673	1.4859	$2.38 \times 10^{-5}$	-10.648
678	1.4749	$3.36 \times 10^{-5}$	-10.302
683	1.4641	$3.95 \times 10^{-5}$	-10.140
688	1.4535	$5.85 \times 10^{-5}$	-9.747
693	1.4430	$8.36 \times 10^{-5}$	-9.389
698	1.4327	$9.55 \times 10^{-5}$	-9.257
703	1.4225	$1.33 \times 10^{-4}$	-8.924
708	1.4124	$1.92 \times 10^{-4}$	-8.560
713	1.4025	$2.17 \times 10^{-4}$	-8.436
718	1.3928	$2.85 \times 10^{-4}$	-8.164
723	1.3831	$3.54 \times 10^{-4}$	-7.945
728	1.3736	$5.31 \times 10^{-4}$	-7.541
733	1.3643	$7.26 \times 10^{-4}$	-7.228
738	1.3550	$9.46 \times 10^{-4}$	-6.963

\* Error in determining the values of the rate constants was no more than 5%.

The rate constant  $k_6$  for 4-IPP  $\rightarrow$  4-NPP isomerization has the highest value, which confirms the predominance of isomerization transformations of branched substituents on the aromatic core during the thermolysis of 4-TBP.

# Calculation of the Arrhenius Parameters

A kinetic analysis of the experimental data in the range of 673-738 K was performed for the "4-TBP  $\rightarrow$ 

products" decomposition reaction using the equations for calculating the first-order reaction rate constant:

$$A \to B$$
, where  $A - 4$ -TBP,  
 $B - \Sigma$ (products), (8)

$$r = kC_A,\tag{9}$$

$$\ln \frac{C_{A,0}}{C_A} = kt. \tag{10}$$

The activation energy and the pre-exponential factor were obtained by linearizing the Arrhenius equation in the  $\ln k_i$ -1000/*T* coordinates:

$$k = A \exp\left(\frac{-E_{\rm a}}{RT}\right). \tag{11}$$

The values of the constants for the "4-TBP  $\rightarrow$  products" decomposition reaction are given in Table 2, the ln  $k_i$ -1000/*T* plot is shown in Fig. 6:

According to the experimental values of the rate constants, the parameters of the Arrhenius equation were calculated: in the temperature range under study, the pre-exponential factor for the "4-TBP  $\rightarrow$  products" decomposition reaction is  $k_0 = 10^{13.2 \pm 0.3}$ , and the activation energy of 4-TBP degradation is 229.9 ± 4.1 kJ/mol.

The Arrhenius parameters were calculated for all the reactions, included in the kinetic model of the process, in the temperature range of 673–738 K (Table 3).

In order to establish the allowable temperature range for syntheses, isolation, operation, and storage of 4-TBP, as well as the duration of its stay under the given conditions, we made an approximate estimate of the 4-TBP stability duration. By the duration of stability, we mean the time during which 1 mol % of the substance degrades at a given temperature (Table 4). The calculation was made on the basis of the obtained values of the activation energy and the rate constant by Eq. (12):

Reaction		k <sub>i</sub>	$k_0,  { m s}^{-1}$	$E_{\rm a}$ , kJ/mol	R	т
4-TBP	4-IBP	<i>k</i> <sub>1</sub>	$12.8\pm0.4$	$224.9\pm4.7$	0.99	14
4-TBP	Phenol	<i>k</i> <sub>2</sub>	$15.7\pm0.2$	$273.7\pm2.8$	0.99	14
4-IBP	4-IPP	<i>k</i> <sub>3</sub>	$17.9\pm0.5$	$299.7\pm6.7$	0.99	14
4-IBP	4-MeP	$k_4$	$18.3\pm0.5$	$303.1\pm6.1$	0.99	14
4-IPP	4-NPP	<i>k</i> <sub>5</sub>	$13.0 \pm 0.1$	214.1 ± 1.9	0.99	14
4-NPP	4-EP	<i>k</i> <sub>6</sub>	$15.8 \pm 0.2$	$260.8\pm2.8$	0.99	14

**Table 3.** Parameters of the Arrhenius equation for thermal transformations accompanying 4-TBP degradation in the rangeof 673–738 K



**Fig. 6.** Plot of the logarithm of rate constant versus the inverse temperature for 4-*tert*-butylphenol decomposition reactions.

**Table 4.** The duration of 4-TBP stability in the temperaturerange 523-773 K

Т, К	Time	Measurement unit
773	2	S
723	25	S
673	428	S
623	3	h
573	6	days
523	2	years

$$\tau = \frac{0.01}{k_0 e^{-E/RT}}.$$
 (12)

## **CONCLUSIONS**

As a result of the study, it has been found that in the temperature range of 673-738 K, the thermolysis of 4-tert-butylphenol proceeds in two directions: dealkylation with the formation of phenol and isomerization into 4-isobutylphenol. At the same time, the isomerization rate significantly prevails, and 4-isobutylphenol is the main product of the transformations studied. The reaction mass was also represented by 4-methylphenol, 4-isopropylphenol, 4-*n*-propylphenol, and 4-ethylphenol.

A kinetic model of 4-TBP thermal transformations that adequately describes the experimental data in the entire temperature range of the study was proposed. For six reactions constituting the kinetic model, the rate constants and the values for the Arrhenius parameters were obtained., For the "4-TBP  $\rightarrow$  products" decomposition in the temperature range of 673–738 K, the rate constants, the activation energy ( $E_a = 229.9 \pm 4.1 \text{ kJ/mol}$ ), and the pre-exponential factor ( $k_0 = 10^{13.2 \pm 0.3}$ ) were determined. On the basis of the data, time intervals in which 99% of 4-TBP retains its stability at a given temperature were approximately estimated. The kinetic parameters were calculated for all the transformations included in the kinetic model.

This information can be used in the development of promising areas of 4-TBP application as a stabilizer or antioxidant for lubricants or polymers operating at elevated temperatures. In general, the known information on the thermal stability of 4-TBP contributes to a more reasonable approach to its use as an additive that increases the oxidative stability of fuels and lubricants, as well as an antioxidant for polymer formulations.

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