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# COMPENSATION EFFECT IN THE KINETICS OF SPATIALLY HINDERED PHENOLS

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## Abstract

This paper reports a linear relationship between kinetic characteristics from the Arrhenius equation describing a decomposition process found when studying the kinetics of thermolysis of spatially hindered phenols. This relationship between the coefficients is known in the literature as a 'compensation effect'. The existence of the compensation effect permits some conclusions concerning the decomposition mechanism and thermal characteristics of the compounds under investigation.

**Keywords:** activation energy, compensation effect, enthalpy, entropy, pre-exponential factor

## Introduction

To clarify the possible use of spatially hindered phenols (SHP) as stabilizers in polymers and plastics their thermal stability in the process of decomposition was studied. Also the kinetic characteristics of some SHP were studied by analyzing thermogravimetric curves using a computational program 'THERMOGRAPH' [1]. Since decomposition takes place during fusion, it is possible to use an equation describing the kinetics of a homogeneous process:

$$d\alpha/dt = k(1-\alpha)^n, \qquad (1)$$

where $\alpha$ – degree of substance conversion, $t$ – time, $n$ – reaction order.

The activation energy ($E$), pre-exponential factor ($Z$) and reaction order ($n$) were calculated from the Arrhenius equation describing the rate constant of decomposition ($k$) as a function of the temperature ($T$):

$$k = Ze^{-E/RT} \qquad (2)$$

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This work considers the relationship between the activation energy and the pre-exponential factor found when studying the kinetic characteristics of SHP. This relationship can be represented for the logarithm of $Z$ as a linear function of $E$:

$$\ln Z = aE + b, \tag{3}$$

which is known in the literature as a compensation effect (CEF).

Such effects were first found for heterogeneous catalytic processes [2, 3]. Later compensation effects were observed in other chemical [4–6] and physico-chemical processes involving reactions in the condensed phase [7–10].

No justified explanations for CEF are found in the literature. This question is discussed in [11–21]. Thus, Roghinsky and Hight [16] attempted an explanation for CEF basing on a number of general quantum-statistical grounds invoking here a nucleus model. They have suggested that 'compensation' in general is inherent to all activation phenomena taking place in condensed media. Lichtenstein [17] has explained CEF anticipating that an activation process is characterized by not only one discrete activation energy value, but by an energy band with Boltzman distribution over the activation barrier value and probability. But this assumption did not find an experimental support. Other authors attribute CEF to processes yielding charged species and radicals [18].

CEF was found in organic chemistry for instance when studying the kinetics of the thermal decomposition of organic compounds in different solvents at varying temperatures [22–24] as well as in photochemical reactions of the generation of enantiomers [25]. Most papers notice a linear relationship between activation entropy $\Delta S^*$ and activation enthalpy $\Delta H^*$ [26, 27]. The equation describing the pre-exponential factor $Z$ is known to include a factor incorporating $\Delta S^*$, and the activation energy depends on the heat of reaction as well. $\Delta S^*$ ($Z$) value receives insufficient attention in many papers dealing with polarization phenomena of atomic interactions. We think that ignoring its changes when passing from one reaction to another [28, 29] is not justified. The predominant formation of ortho- and para-derivatives taking place due to a large number of active state variants should be related to this kinetic factor, not to the activation energy value only. Roghinsky thinks [30] that the most likely reason for the wide variations of the pre-exponential factor is the influence of steric factors and changes in transition state polarity. In his opinion the occurrence of CEF in reactions of phenols is attributable to the fact that the rate constants under consideration are effective values and do not refer to an elementary chemical act. This is evidenced by the observed compensation effect accompanied by wide pre-exponent variations. The specific reason for the 'non-elementariness' of experimentally measured rate constants is the participation of activated complexes in the reactions. The analysis of kinetic schemes involving these complexes shows that $E$ and $Z$ indexes are more sensitive to the 'non-elementariness of the process' than the absolute values of the rate constants [30].

# Experimental

This paper represents a study of 21 SHP demonstrating CEF. The reaction rate for most of the compounds studied differs from one and equals 2, 3 and even more. This is indicative of a decomposition complex nature with several processes taking place concurrently [1]. Figure 1 represents two straight lines (I, II) referring to the dependence of ln*Z* on *E* (Eq. (3)). Tables 1 and 2 also show the values of ln*Z*, *E* and ln*k* in relation to the decomposition start temperature ($T_1$) and maximum decomposition temperature ($T_2$). Data shown in Tables 1 and 2 are calculated from the experimental curves taken from [31] using the method described in [1]. The represented data exhibit theoretical relations between the enthalpy (*E*) and entropy (*Z*) components of input into the kinetic stability of SHP. The two straight lines in Fig. 1 indicate that the compounds under investigation are divided into two groups having distinct thermolysis mechanisms. The decomposition reaction rate depends on the enthalpy and entropy input in the process (lines I and II on Fig. 1).

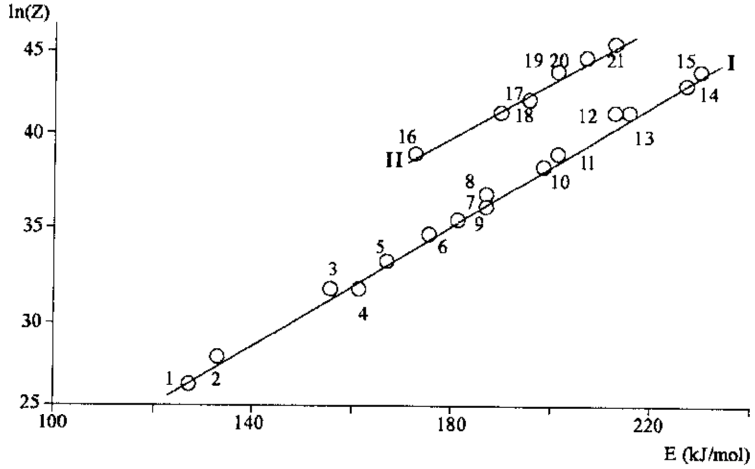


**Fig. 1** Dependence of ln(*Z*) upon *E*

An analysis of the dependence of ln*k* on the temperature (1/*T*) (Fig. 2) proves that for the SHP under investigation there is an isokinetic temperature at which compounds have identical decomposition rates. For the set of compounds resting on straight line I (Fig. 1) this temperature equals 410°C (±5°), and ln*k*=5.3 (±0.1). For the compounds resting on line II the above temperature corresponds to ln*k*=9.3, and the isokinetic temperature is 438°C (±5°) appropriate to ln*k*=10.3. In other words, at the same temperature the compounds resting on line II have decomposition rates four orders of magnitude higher than those on line I. For the compounds found on the same line an increase in the entropy factor by one order of magnitude corresponds to an increase in the activation energy by about

**Table 1** Kinetic parameters of SHP

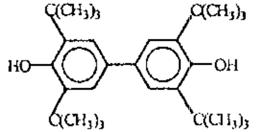
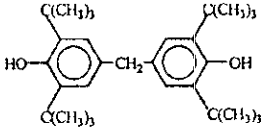
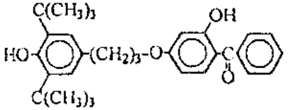
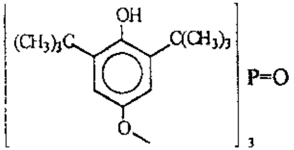
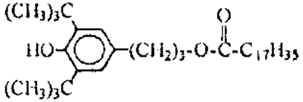
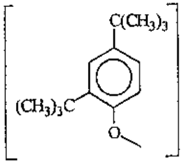
| Compound | Formula | $T_1$/°C | $T_2$/°C | $E$/kJ mol$^{-1}$ | ln$Z$ | ln$k_1$ | ln$k_2$ |
|---|---|---|---|---|---|---|---|
| 3,3',5,5'-Tetra-tert-butyl-4,4'-hydroxybiphenyl |  | 195 | 325 | 128.4 | 26.80 | –6.26 | 1.0 |
| Di-(3,5-di-tert-butyl-4-hydroxyphenyl)-methane |  | 160 | 310 | 132.4 | 27.51 | –9.27 | 0.13 |
| 4-[3-(3,5-Di-tert-butyl-4-hydroxyphenyl)-propoxy]-2-hydroxybenzophenone (BENZON-P) |  | 260 | 400 | 156.7 | 31.74 | –3.72 | 3.64 |
| Tris-(3,5-di-tert-butyl-4-hydroxyphenyl)-phosphate (PHENOZAN-50) |  | 275 | 355 | 164.8 | 32.66 | –3.39 | 1.15 |
| 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propyl-stearate |  | 290 | 410 | 182.3 | 35.88 | –3.28 | 3.76 |
| Tris-(2,4-di-tert-butyl-phenyl)-phosphite |  | 180 | 365 | 187.9 | 36.60 | –13.35 | 1.12 |

**Table 1** Continued

| Compound | Formula | $T_1$/°C | $T_2$/°C | $E$/kJ mol$^{-1}$ | ln$Z$ | ln$k_1$ | ln$k_2$ |
|---|---|---|---|---|---|---|---|
| Di-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propyl]sulphide (SO-3) | | 220 | 310 | 172.0 | 34.45 | –7.55 | –1.04 |
| 2-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid-2,2'-oxybisethanol-diester (PHENOZAN-28) | | 240 | 310 | 184.9 | 36.60 | –6.79 | –1.67 |
| Di-(3-tert-butyl-4-hydroxyphenyl)sulphide | | 225 | 330 | 187.9 | 37.03 | –8.40 | –0.49 |
| 2-[(3,5-Di-tert-butyl-4-hydroxyphenyl)propyl-thio]benzothiazol | | 225 | 330 | 195.0 | 37.97 | –9.18 | –0.97 |
| 1,1',3-Tris-(3.5-di-tert-butyl-4-hydroxyphenyl)propane | | 240 | 330 | 197.4 | 38.64 | –7.65 | –0.77 |
| 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propyl-palmitate | | 225 | 350 | 211.1 | 40.92 | –7.07 | 0.04 |

**Table 1** Continued

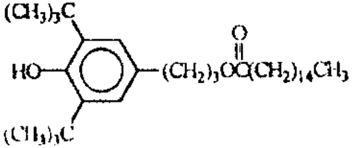
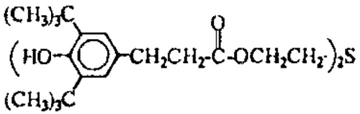
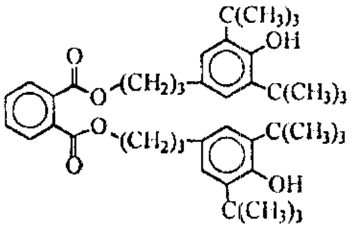
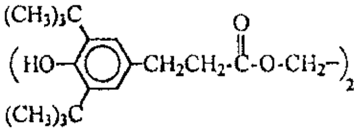
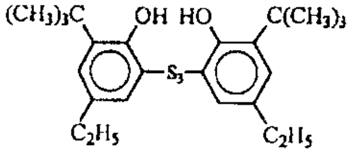
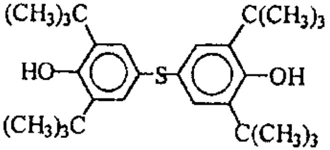
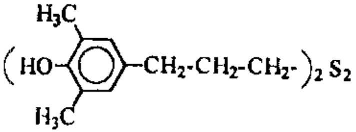
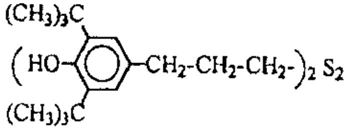
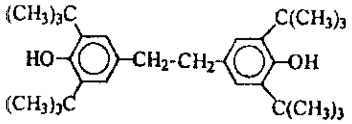
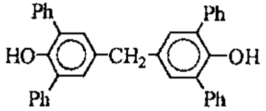
| Compound | Formula | $T_1$/°C | $T_2$/°C | $E$/kJ mol$^{-1}$ | lnZ | ln$k_1$ | ln$k_2$ |
|---|---|---|---|---|---|---|---|
| 3-(3,5-Di-tert-butyl-4-hydroxy phenyl)-propyl-palmitate |  | 255 | 350 | 211.1 | 40.92 | –7.07 | 0.04 |
| 2-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid-2.2'-thiobisethanol-diester (PHENOZAN-30) |  | 280 | 350 | 212.6 | 41.22 | –5.06 | 0.05 |
| Di[2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethyl]-phthalate (PHENOZAN-42) |  | 280 | 350 | 225.4 | 43.00 | –6.09 | –0.66 |
| 2-(3,5-Tert-butyl-4-hydroxyphenyl)propionic acid-1,2-ethanedioldiester (PHENOZAN-27) |  | 245 | 365 | 228.1 | 43.50 | –9.46 | 0.42 |

**Table 2**

| Compound | Formula | $T_1$/°C | $T_2$/°C | $E$/kJ mol$^{-1}$ | ln$Z$ | ln$k_1$ | ln$k_2$ |
|---|---|---|---|---|---|---|---|
| Bis-(3-ethyl-5-tert-butyl-6-hydroxyphenyl)-trisulphide |  | 180 | 275 | 176.0 | 39.00 | –7.64 | 0.84 |
| Bis-(3,5-di-tert-butyl-4-hydroxyphenyl)-sulphide |  | 180 | 295 | 190.1 | 41.31 | –8.98 | 1.10 |
| Di-[3-(3,5-dimethyl-4-hydroxyphenyl)propyl]disulphide |  | 220 | 295 | 197.5 | 42.50 | –5.80 | 0.61 |
| Di-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl]disulphide (SO-4) |  | 220 | 295 | 203.8 | 43.38 | –6.38 | 0.24 |
| Bis-1,2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethane |  | 220 | 305 | 208.0 | 44.25 | –7.29 | 0.33 |
| 4,4'-Bis-(3,5-diphenyl-4-hydroxyphenyl)methane |  | 340 | 435 | 214.8 | 45.24 | 3.12 | 8.81 |

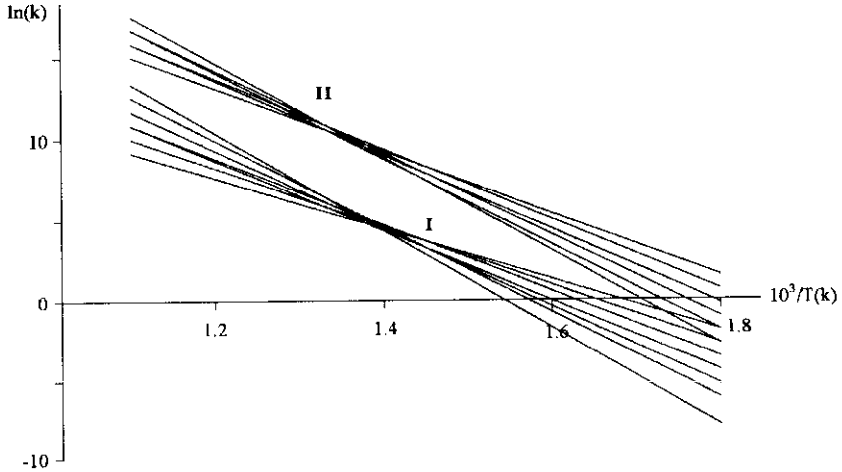


**Fig. 2** Dependence of ln(*k*) upon 1/*T*

6 kJ mol$^{-1}$ (1.44 kcal mol$^{-1}$). Relying on the curves given in Fig. 2 it should be noted that the reaction rate is specified by changes in the energetic barrier (the value of activation energy) below the isokinetic temperature, and by the entropy factor (the value of pre-exponential factor) characterizing steric hindrances in the formation of intermediate state above this temperature. This is evident from data in the given tables, where ln$k_1$ corresponds to the reaction rate at temperature $T_1$ (decomposition start), and ln$k_2$ – to the reaction rate at $T_2$ (maximum decomposition), taken from experimental data from [31]. The RSD of the results tabulated is 4% for *E* and *T*, and 1% for lnZ and ln*k* with a confidence interval of 0.95.

## Conclusions

When analysing the values of activation energy and pre-exponential factor for a large set of compounds under investigation, a so-called compensation effect has been found. The compounds under investigation were divided into two groups with distinct isokinetic temperatures. The obtained constants are understood to be effective values and not to correspond to an elementary act, however, for a large series of similar organic compounds (SHP) studied under standard experimental conditions we think the experimentally observed correlations between *E* and *Z* are not accidental.

Isoenthalpy and isoentropy series were not found, only the ones with a compensation effect were observed, that is why dividing similar organic compounds into two groups based on their decomposition kinetics can be considered as indicating two distinct chemical mechanisms limiting the process stages (for example, the presence or absence of concurrent-consecutive reactions). Such division is hardly predictable based on their molecular structures only (Tables 1 and 2).

This suggests that further similar research on the thermal decomposition of organic compounds used as polymer stabilizers may be promising. Such a systematic set of kinetic information (but not only choosing the most promising samples by their initial decomposition temperature) will actually give an opportunity of linking the indexes required for stabilizers to the significant quantitative characteristics of their reactivity in pyrolysis. This will be helpful in the search for new compounds of predictable properties.

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