# THERMOGRAVIMETRIC ANALYSIS OF INCLUSION COMPOUNDS OF PERHYDROTRIPHENYLENE WITH HIGHER n-ALCOHOLS

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The vaporization of perhydrotriphenylene and its inclusion compounds with higher even-numbered n-alcohols from $C_8$ to $C_{16}$ has been studied using thermogravimetric analysis. For the inclusion compounds of perhydrotriphenylene with the $C_8$, $C_{10}$ and $C_{12}$ n-alcohols, kinetic analysis shows that the vaporization processes of the n-alcohol and the perhydrotriphenylene are partially superimposed, while for the inclusion compound perhydrotriphenylene-hexadecanol-1, the above processes are totally superimposed. From the experimental kinetic parameters the values of the preexponential factors corresponding to the vaporization of the n-alcohols and perhydrotriphenylene were calculated, as were the compositions of the inclusion compounds of perhydrotriphenylene with the $C_8$—$C_{12}$ n-alcohols.

The *anti-trans-anti-trans-anti-trans* equatorial isomer of perhydrotriphenylene (PHTP), $I_a$ and $I_b$, forms stable channel-like inclusion compounds with hydrocarbons, alcohols, esters, monocarboxylic acids, macromolecules, etc. [1—4]. Within the channels which penetrate the structures of the PHTP inclusion compounds, long-chain guest molecules are isolated from one another longitudinally by the channel walls, but end-group interactions between successive chains are permitted, affording a means of comparing these interactions in different homologous series through their contribution to the thermal stability of the inclusion compound.

The thermal decompositions of the inclusion compounds PHTP — higher even-numbered n-alcohols from $C_8$ to $C_{18}$, studied by differential thermal analysis [5], revealed that their stabilities become higher as the chain length of the included alcohol increases.

This paper deals with a study of the thermal vaporization processes of PHTP and its inclusion compounds with even-numbered aliphatic alcohols from $C_8$ and $C_{16}$, using thermogravimetric analysis.

## Experimental

The inclusion compounds PHTP — n-alcohols were prepared by mixing saturated solutions of PHTP and n-alcohols, $C_8$—$C_{16}$, in methyl ethyl ketone, at 60—70°, followed by slow-cooling crystallization at room temperature as previously described [5].

Inclusion compound formation was proved by I.R. spectrometry, X-ray diffraction and thermal analysis.

The samples were analyzed on a Paulik—Paulik—Erdey derivatograph, in air, using 50 mg substance, at a heating rate of 12 degree/min.

## Results and discussion

The DTA curves of PHTP and the investigated inclusion compounds PHTP — n-alcohols clearly demonstrate that the loss in weight begins after their melting.

### a) PTHP

The loss in weight begins at 122° (Fig. 1). The curves indicate the existence of two processes, I and II. The former process, representing about 95% of the total loss in weight, ends at about 360°, and the latter process begins at approximately 360° and ends at 550°. Kinetic analysis also indicates that the former process consists principally in vaporization without decomposition of PHTP. Only in the final part of this process does the high temperature make possible the occurrence of a thermal decomposition process: decomposition of a residue stable up to 550°.
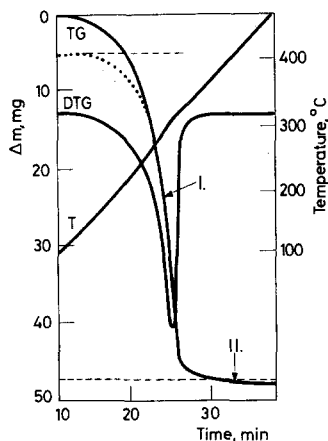


**Fig. 1** Thermoanalytical curves of the inclusion compound PHTP —dodecanol-1. The dotted line represents the separation by calculus of the PHTP vaporization process

### b) Inclusion compounds PHTP — n-alcohols

In this case too the loss in weight begins at 122° and the thermal curves indicate the same processes as above. A final process controlled by the thermal decomposition of PHTP was identified at high temperature, similarly as for pure PHTP decomposition.

c) *Kinetic analysis*

Kinetic analysis of the above vaporization processes was carried out by using several methods, e.g. those of Coats and Redfern, Freeman and Carrol [6] and Reich *et al.* [7]. All these methods indicated a zero-order reaction for almost the entire process, which confirms our hypothesis that a vaporization process takes place.

The ploots In (DTG) *vs.* $1/T$ allow determination of the values of $Z$ and $E$ in the Arrhenius equation. In the case of PHTP (Fig. 2), the graph indicates the existence of certain unique parameters $Z$ and $E$. For the i. clusion compounds PHTP — *n*-alcohols, $C_8-C_{12}$, the graphs consist of two straight line segments, the one at low temperatures being attributed to *n*-alcohol vaporization and that high temperatures to PHTP vaporization. As an example, in Fig. 3 In (DTG) is plotted *vs.* $1/T$ for the inclusion
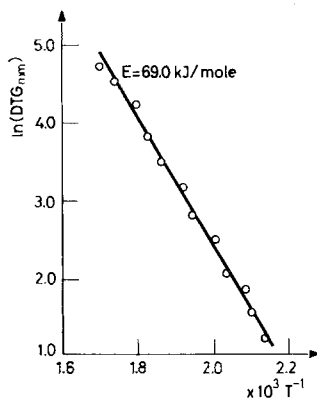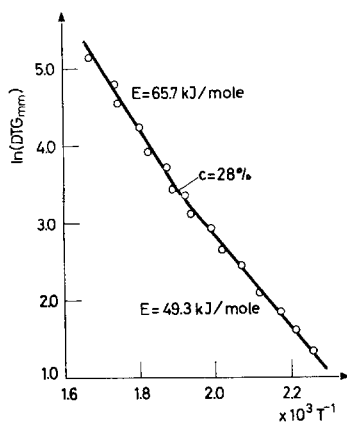
Fig. 2 In (DTG) *vs.* $1/T$ for PHTP

Fig. 3 In (DTG) *vs.* $1/T$ for the inclusion compound PHTP — dodecanol-1

**Table 1** Kinetic parameters of components in inclusion compounds

| Inclusion compound | n-Alcohol | | PHTP * | |
|---|---|---|---|---|
| | $Z$, min$^{-1}$ · $10^{-5}$ | $E$, kJ mol$^{-1}$ | $Z$, min$^{-1}$ · $10^{-5}$ | $E$, kJ mol$^{-1}$ |
| PHTP — octanol-1 | 0.26 | 45.6 | 3.8 | 66.9 |
| PHTP — decanol-1 | 0.23 | 36.0 | 3.8 | 66.9 |
| PHTP — dodecanol-1 | 0.59 | 49.3 | 3.0 | 65.7 |
| PHTP — hexadecanol-1 | $Z = 4.6 \cdot 10^5$ min$^{-1}$; $E = 67.7$ kJ mol$^{-1}$ | | | |

*PHTP in pure state: $Z = 4.98 \cdot 10^5$ min$^{-1}$; $E = 69.0$ kJ mol$^{-1}$.

compound PHTP — dodecanol-1. In such a representation the inclusion compound PHTP — hexadecanol-1 exhibits only a straight line. This behaviour demonstrates the tendency of the two vaporization processes to be more and more superimposed as the chain length of the guest molecule increases.

The above graphs allowed determination of the experimental kinetic parameters $E$ and $Z_{exp.}$ corresponding to the two processes. From these values, a theoretical separation of the two processes was attempted. The aims of this attempt were to determine the preexponential factors $Z$ (min$^{-1}$) with kinetic meaning, and to test the possibility of thermogravimetric determination of the compositions of the inclusion compounds.

To present the technique of their separation by calculus, it is necessary to employ the corresponding kinetic equations. In our case, we write

$$\frac{dC}{dt} = Z \cdot e^{-E/RT}. \tag{1}$$

Taking into account that

$$C = 1 - \frac{W}{W_0}$$

where $W$ is the weight at instant $t$, ad $W_0$ is the total weight associated with the respective process, Eq. (1) can be written

$$\frac{dW}{dt} = -Z_{exp.} \cdot e^{-E/RT} \tag{2}$$

where $Z_{exp.} = Z \cdot W_0$.

Integrating Eq. (2) for constant heating rate, $\beta = dT/dt$, we obtain

$$W_0 - W = \frac{Z_{exp.} \cdot E}{\beta R} p(x) \tag{3}$$

where $x = E/RT$ and $p(x) = \int_x^\infty \frac{e^{-u}}{u^2} \, du.$

The function $p(x)$ defined as above is called the "temperature integral" in the literature [8].

By means of Eq. (3) the $W_0$ associated with PHTP vaporization was determined for the inclusion compounds PHTP with octan-1, decanol-1 and dodecanol-1, $W$ being selected from the region where superimposition does not take place.



I a.            I b.
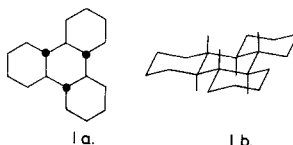
Separation in the case of the inclusion compound PHTP — dodecanol-1 is represented in Fig. 1. The $W_0$ corresponding to the vaporization process of the $n$-alcohol is obtained by difference. By using the values found as above, the preexponential factors and compositions of the respective inclusion compounds found by this method are in good agreement with those found by elemental chemical analysis (Table 2).

According to the kinetic theory [9], the vaporization enthalpies of alcohols, $\Delta H_v$, can be calculated by using the equation

$$\Delta H_v = E + \frac{3RT}{2} \qquad (4)$$

where $E$ is the experimental activation energy, kJ mol$^{-1}$. Thus, for octanol-1, at the mean temperature of our experiment, $T_m = 150°$, and $E = 45.6$ kJ mol$^{-1}$, using Eq. (4) we get $\Delta H_v = 51.0$ kJ mol$^{-1}$. This value is in good agreement with that found by using the following empirical equation [10]

$$\Delta H_v = 10 + 2.2\,n - (2.5 + 1.88\,n)RT \qquad (5)$$

where $n$ is the number of chain carbon atoms in the alcohol and $R$ is the universal gas constant in kcal. $K^{-1}$ mol$^{-1}$.

For comparison, a mean temperature must always be adopted. Thus, if $n = 16$, and $T_m = 200°$, Eq. (5) gives $\Delta H_v = 61.1$ kJ mol$^{-1}$.

**Table 2** Compositions of inclusion compounds PHTP — $n$-alcohols

| Inclusion compound | Elemental analysis | | | | Weight ratio PHTP/$n$-alcohol, by TG |
| --- | --- | --- | --- | --- | --- |
| | C% | H% | O% | Weight ratio PHTP/$n$-alcohol | |
| PHTP — octanol-1 | 86.72 | 12.21 | 1.07 | 10.42 | 9.89 |
| PHTP — decanol-1 | 86.87 | 12.24 | 0.89 | 10.26 | 11.11 |
| PHTP — dodecanol-1 | 86.96 | 12.27 | 0.77 | 10.15 | 11.03 |
| PHTP — hexadecanol-1 | 87.13 | 12.28 | 0.59 | 10.18 | — |

**Conclusions**

Our results may be summarized as follows:

1. The TG curves of PHTP and the inclusion compounds PHTP — $n$-alcohols indicate principally vaporization processes up to 360°; above this temperature another process occurs, the decomposition of a residue stable up to 550°.

2. Kinetic analysis of the data shows that the vaporization process of $n$-alcohol and PHTP are partially superimposed for all the studied inclusion compounds except PHTP — $n$-hexadecanol-2, for which the vaporization processes are totally superimposed.

3. From the experimental kinetic parameters, the values of the preexponential factors corresponding to vaporization of the $n$-alcohols and PHTP, as well as the compositions of the inclusion compounds of PHTP with the $n$-alcohols, $C_8 - C_{12}$, have been calculated. The compositions determined thermogravimetrically, by theoretical separation of the two processes, agree satisfactorily with the values obtained by chemical analysis.

**References**

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**Zusammenfang** — Die Verdampfung von Perhydrotriphenylen und dessen Einschlussverbindungen mit höheren geradzahligen $n$-Alkoholen von $C_8$ bis $C_{16}$ wurde thermogravimetrisch untersucht. Die kinetische Analyse ergab, dass sich die Verdampfungsprozesse des $n$-Alkohols und Perhydrotriphenylens bei Einschlussverbindungen von Perhydrotriphenylen mit $n$-Alkoholen von $C_8$ bis $C_{12}$ teilweise, bei der Einschlussverbindung Perhydrotriphenylen-Hexadecanol-1 dagegen vollständig überlagern. Aus den experimentellen kinetischen Parametern wurden sowohl die sich auf die Verdampfung der $n$-Alkohole und des Perhydrotriphenylens beziehenden präexponentiellen Faktoren als auch die Zusammensetzungen der Einschlussverbindungen von Perhydrotriphenylen mit den $n$-Alkoholen von $C_8$ bis $C_{12}$ berechnet.

**Резюме** — Используя термогравиметрический анализ было изучено испарение пергидротрифенилена и его клатратных соединений с нормальными спиртами с четным числом углеродных атомов от $C_8$ до $C_{16}$. Для клатратов пергидротрифенилена с н-спиртами с числом углеродных атомов $C_8$, $C_{10}$ и $C_{12}$ кинетический анализ показал, что процессы испарения н-спирта и пергидротрифенилена частично перекрываются, в то время как для клатрата пергидротрифенилен — гексадеканол-1 — процессы полностью перекрываются. На основе экспериментальных кинетических параметров были вычислены значения предэкспоненциальных факторов процесса испарения н-спиртов и пергидротрифенилена, а также состав клатратных соединений пергидротрифенилена с $C_8 - C_{12}$ н-спиртами.