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Solid Rotator Phases in 2,2,4,4- Tetramethyl-3-t-butyl-pentane-3-ol (t-Bu$_3$ COH)

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Solid Rotator Phases in 2,2,4,4-Tetramethyl-3-t-butyl-pentane-3-ol (t-Bu_3COH)

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The infra-red spectroscopy, proton magnetic resonance, dielectric measurements and differential thermal analysis methods were employed to investigate solid 2,2,4,4-tetramethyl-3-t-butyl-pentane-3-ol (TTBC). TTBC was found to appear as a monomer in solid state which creates favourable conditions for molecular rotation with the spherical structure of molecules. Temperature existence ranges for internal and molecular rotator phases have been determined.

INTRODUCTION

The potential energy of a molecule is changed as a result of interactions with its neighbours in the molecular crystal as its orientation is altered. The energy barrier between various equilibrium states would determine to what extent the molecule rotation may acquire the nature of free or restricted rotation or only of torsional vibration. Particularly low barriers would appear in case if two conditions are satisfied:

1) geometrical condition–approximately spherical molecules
2) energy condition–absence of specific intermolecular interactions.

These conditions occur simultaneously, e.g. in many halogeno, nitro and cyano-derivatives of methane[1-4]. On the other hand, in the case of associated compounds which contain proton-donor hydroxyl or amino groups, the molecular rotation would require an additional energy expense of about 5-6 kcal/mole per one hydrogen bond.

These difficulties may be, however, circumvented by introducing sufficiently large substituents which hinder the self-association processes, into α-positions with respect to the proton-donor group. 2,2,4,4-tetramethyl-3-t-butylpentane-3-ol has not been hitherto examined from point of view[5, 12-15]. Screening of hydroxyl groups by the three bulky t-butyl substituents is so effective that TTBC remains monomeric even in the solid phases. The hydroxyl groups are, however, so accessible that intermolecular hydrogen bonds with simple proton acceptors may be formed[5] as in the case of 2,2,4,4-tetramethyl-pentane-3-ol[6].

EXPERIMENTAL TECHNIQUES

TTBC has been synthesized and described by L. Syper[7]. The compound was purified by recrystallization from methanol and its purity was checked by vapor-phase chromatography(M.p. 118±0,5°C). The IR absorption spectra have been measured in Perkin-Elmer Model 220, 125 and 621 spectrophotometers using a low-temperature attachment†. Thin layers obtained by fusing and cooling down alcohol between the KBr plates.

The proton magnetic resonance measurements have been made in a Varian Model DP 60 lowresolution spectrometer for solids‡.

The dielectric constant and dielectric losses measurements up to 25 MHz were made in a MQL-18 Q-meter using a capacitor of our own design. The DTA and DTG curves were recorded in an OD-102 derivatograph.

RESULTS AND DISCUSSION

The following rotary motions are possible for TTBC:

1) molecular rotation in the high-temperature solid phase
2) internal rotation of hydroxyl groups
3) internal rotation of methyl groups
4) internal rotation of t-butyl groups.

It seems probable that the internal rotations of groups over certain temperature ranges may be mutually coupled owing to their adjacent positions. The

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† The IR absorption spectra have been measured at Prof. R. Freymann's Laboratory – Paris.

‡ The NMR spectra have been measured at Institute of Low Temperature and Structure Research, Polish Academy of Science – Wrocław.

rotary motion of methyl groups engaged with the adjacent groups is a necessary condition for the rotary motion of t-butyl substitutes as a whole.

Four parallel measurement techniques were employed for studies on the dynamics of rotary motions in TTBC.

Differential thermal analysis

Measurements were carried out in a Type OD-102 derivatograph with the sample being heated up and cooled down over the temperature range from 290-400°K. The DTA curve image (Figure 1) enables to find out the presence of two phase transitions. The transition observed at 302°K is of a solid-solid type while that at 391°K is of a solid-liquid type. Assuming that the band surface in the DTA curve is proportional to the amount of heat released, it may be shown that the heat of transition from a low-temperature β-phase to a high-temperature α-phase exceeds the double value of the heat of fusion.

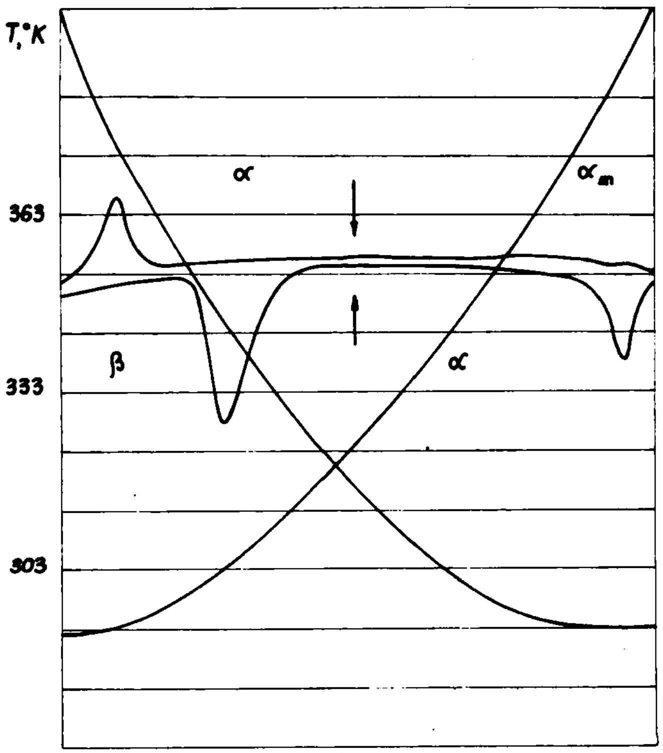

FIGURE 1 DTA curves in the heating and cooling processes of TTBC over the temperature range from 293 to 400°K

TTBC was found to exhibit a strong temperature hysteresis of phase transitions liquid ⟶ plastic phase α and plastic phase $\alpha \longrightarrow$ low-temperature solid phase β. These overcoolings amount to 5-20°K for alcohol solidification and from 1 to 60°K for $\alpha \longrightarrow \beta$ transition. The overcooled plastic metastable α_m phase has properties characteristic of the α-phase.

The amount of overcooling observed during the $\alpha_m \longrightarrow \beta$ transition depends on the cooling rate $\mathrm{d}T/\mathrm{d}t$, sample thickness and its origin. A very strong overcooling effect would be observed when the alcohol sample is at first fused and then slowly cooled off. On the contrary, a weak effect would be observed when the β phase is heated a few degrees above the transition point and then cooled off.

This is why no exothermic $\alpha \longrightarrow \beta$ transition band appears in the temperature range under investigation in the cooling curve (Figure 1).

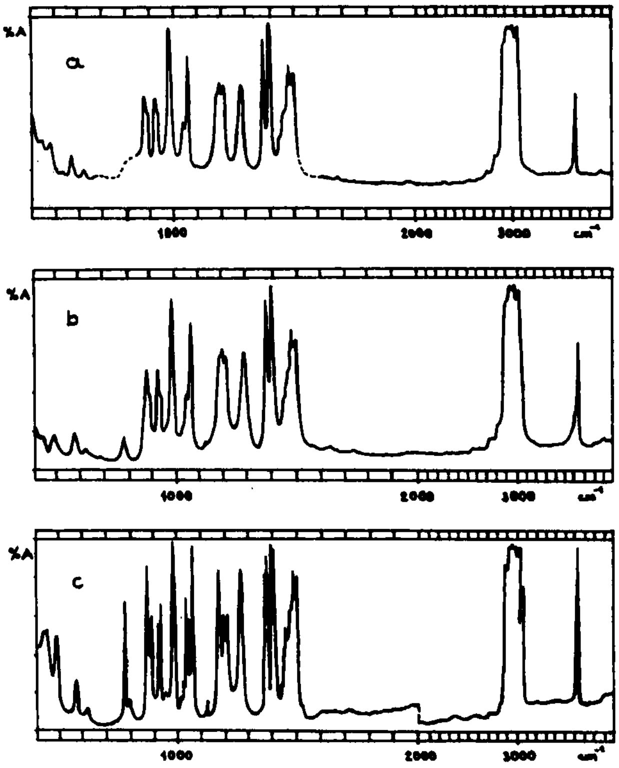

FIGURE 2 Infra-red spectra of TTBC in CCl_4 solution (c = 0,5 m/1, 1 = 0,1 mm) – a, and in solid state (film) at 302°K – b, at 110°K – c

IR absorption spectra

The studies were made on thin alcohol layers over the temperature range from 100 to 320°K. Figure 2 shows IR spectra over the fundamental frequency range from 400-4000 cm^{-1} for TTBC in CCl_4 solution as well as for solid phases: plastic phase at 305°K and frozen phase at 110°K.

The spectra obtained for solutions and for a high-temperature solid phase are almost identical with respect to both positions and intensities of particular bands. This means that the dynamic condition of alcohol molecules is similar in both cases. This is possible only under free molecular rotation in the solid phase.

Typical bands assigned to stretching and deformation frequencies in the hydroxyl group plane are found at 3632 and 1279 cm^{-1}, respectively. Slight differences are observed only in the band contour of the OH group valence vibration frequencies. This band which is almost exactly symmetric in diluted solutions of neutral solvents (below 0,5 mole/l)[5], in the solid phase has two side low-intensity components shifted towards lower frequencies at about 20 and 45 cm^{-1}. The origin of the side bands will be discussed in detail in a separate paper.

The TTBC spectrum undergoes drastic changes in the low-temperature phase as a result of the molecules being mounted in the crystal lattice. The phase transition, and the crystal field effect manifested then result in stepwise ν(OH) and δ(OH) frequency shifts as well as in many splittings and changes in the intensity ratios of particular band components over the 700-1500 cm^{-1} region.

The phase transitions in solid TTBC are accompanied by a complex evolution of the ν(OH) band countour and component intensities. The band evolution is a reversible process—the temperatures of $\alpha \longrightarrow \beta$ and $\beta \longrightarrow \alpha$ phase transitions may be, however, considerably shifted, even up to 60° and, therefore, the frequency scale positions of the corresponding components may also differ near the transition temperatures.

As the temperature of phase α is decreased, a slight shift of the main ν(OH) band component (c) from 3632 to 3629 cm^{-1} is observed—simultaneously the extinction of that component is reduced in favour of (a) and (b) components. The intensity of (a) component reaches its maximum at the $\alpha \rightleftarrows \beta$ phase transition temperature.

The transition is very rapid, particularly in thin sample layers and at excessive overcoolings and hence, it is difficult to maintain the condition in which the two phases would exist.

At the β phase transition temperature, maximum absorption falls at 3606 cm^{-1}, (a) component is still existing and (c) component disappears stepwise.

Further decrease in temperature results in a gradual weakening of the (a) component intensity and then it disappears. Simultaneously the band becomes sharper and symmetric and its frequency increases up to 3608 cm^{-1}.

Thus at about 100°K for the frozen δ phase we have only a single, symmetric band with a considerably lower halfwidth at 3608 cm^{-1}.

The changes in deformation frequency band of the TTBC hydroxyl groups are less complex. Phase α exhibits a single and symmetric δ (OH) band at 1279 cm^{-1}. At the $\alpha \rightleftarrows \beta$ transition temperature the band is stepwise shifted to 1262 cm^{-1}. Further decrease in temperature results in sharpening of the band, increase of its extinction and decrease of its half-width. The position of the band peak remains, however, unchanged. An evolution of the IR absorption spectrum resulting from the temperature changes indicates a complex nature of dynamics in solid TTBC.

Dielectric measurements

The dielectric studies on systems with steric hindrances (alcohols and phenols) in the solid phase were always relating the dielectric absorption to the internal rotation of the hydroxyl group. In the phenols substituted at positions 2, 6 with bulky substituents–the undimerizable hydroxyl groups are, however, free to rotate around the C-O bond[8,9]. The dielectric absorption, described by the

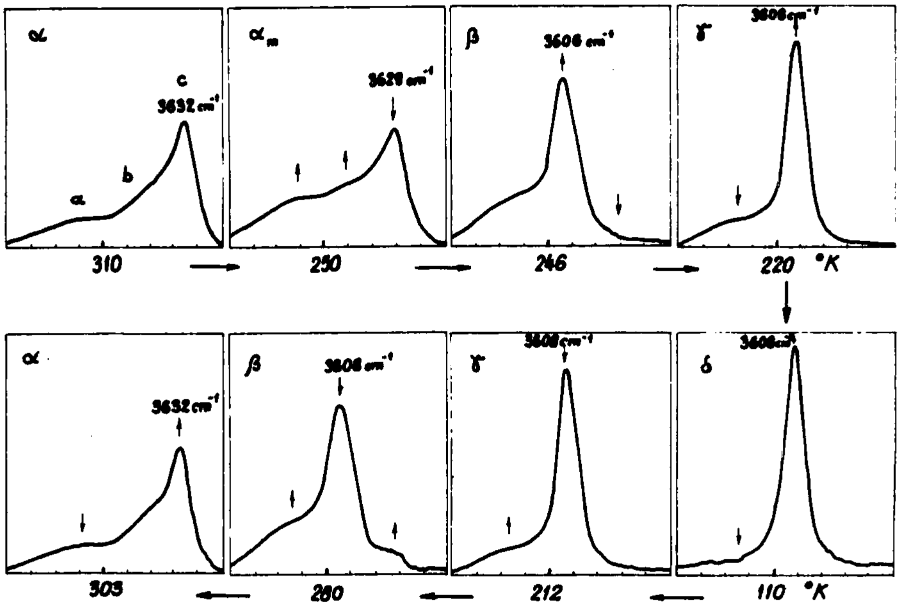

FIGURE 3 Effect of temperature on the band contour of valence frequencies for hydroxyl groups in TTBC (solid film)

Debye curve, is increasing proportionally to 1/T. The energy barriers for various phenol derivatives are of the order of 1-2,5 kcal/mol.

The Meakins' conclusions concerning the alcohols: triphenylcarbinol[10] and tricyclohexylcarbinol[8] do not seem to be fully justified. The higher activation energies, above 4 kcal/mole, result rather from total dimerization in the former case and partial dimerization in the latter case of carbinols in question than from an increased internal friction of hydroxyl groups.

On the other hand, no dielectric absorption related to the occurrence of solid rotator phases was found for phenols and alcohols. The second relaxation time related to the reorientation of the entire molecules could have been observed only for solutions of these coumpounds.[9]

The dielectric absorption in the high and low temperature forms of the aliphatic[11] long-chain[12] alcohols can be explained by a precess involving rotation of the individual–OH groups about the C-O bonds, accompanied by breaking and reforming of the hydrogen bonds.

The results of dielectric studies on TTBC are shown in Figures 4 and 5. A plot of dielectric permittivity versus temperature for the solid phase shows two characteristic phase transitions–one of the I type and another one of the II type. At temperatures below 230°K (phase γ) the dielectric permittivity is close to the optical one $\epsilon'_\infty \simeq 2{,}26$. Under such conditions, the TTBC molecules and their

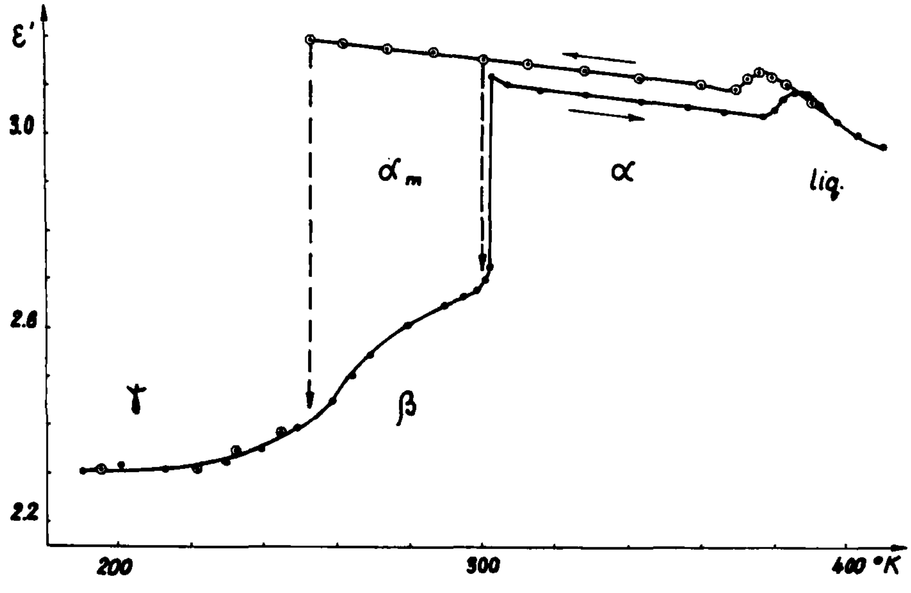

FIGURE 4 Dependence $\epsilon' = f(T)$ at 4 MHz

hydroxyl groups which may contribute to the dielectric relaxation, are frozen. On the other hand, the methyl group rotation occurring at these temperatures could not increase the value of ϵ'.

A second type transition $\gamma \longrightarrow \beta$ is observed above 230°K where the free hydroxyl groups are being gradually unfrozen. This transition is accompanied by a gradual increase in ϵ' up to about 2,65.

Another first type $\beta \longrightarrow \alpha$ phase transition occurs at 302,5°K–with stepwise increase of ϵ' from 2,7 to ab. 3,15. This transition involves heat absorption (Figure 1) and a stepwise shift of the stretching ν(OH) and bending δ(OH) frequencies to higher values (Figures 2 and 3). These facts may be explained only as a result of liberation of the molecular rotation in the solid α phase. This conclusion will become evident when observing the changes in dielectric permittivity with the temperature increasing above the melting point.
Only very small changes in ϵ' are observed near the melting point.

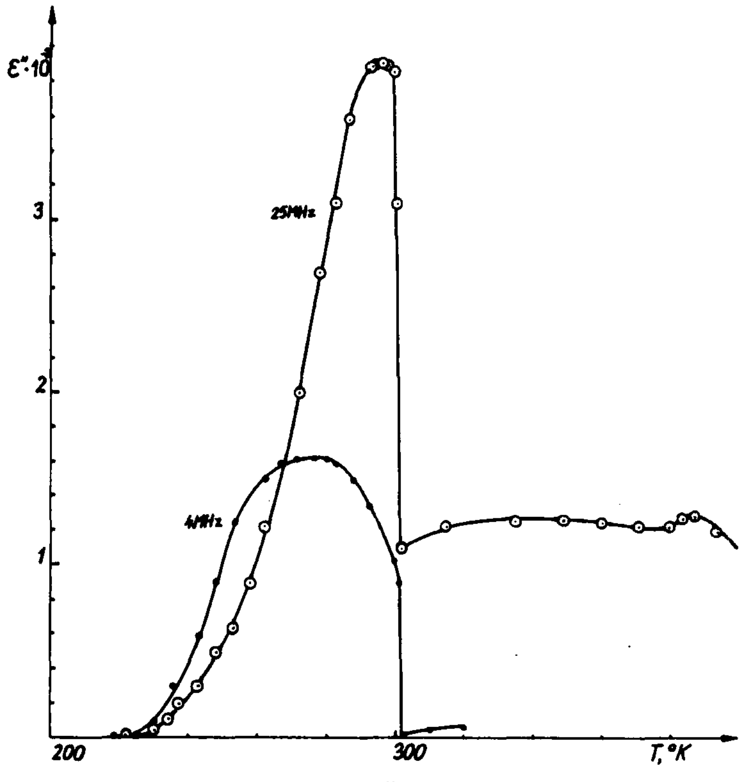

FIGURE 5 Dependence $\epsilon'' = f(T)$ at 4 and 25 MHz

The dielectric measurements have confirmed the occurrence of a temperature hysteresis depending on the history of the sample. It occurs in liquid $\longrightarrow \alpha$ and $\alpha \longrightarrow \beta$ transitions and has not been found for the $\beta \longrightarrow \gamma$ transition.

Starting from the fused substance, a gradual increase in dielectric permittivity is observed with decreasing temperature not only in the solid α phase but also in the overcooled α_m phase (Figure 4). The changes in $\Delta\epsilon'$ ($\alpha_m \longrightarrow \beta$) may be then considerably higher than those of $\Delta\epsilon'(\alpha \rightleftarrows \beta)$.

The dielectric absorption in the high-temperature α phase related to the molecular and internal absorption of hydroxyl groups occurs at frequencies above 10^8 Hz and will be discussed later.

The crystal structure changes in the $\alpha \longrightarrow \beta$ phase transition which are accompanied by considerable limitations of the freedom of movement for the methyl groups (NMR measurements) and freezing of the molecular rotator condition result also in a considerable increase of internal friction for the hydroxyl groups. In consequence, significant dielectric losses occur in the β phase over the MHz frequency region which are assigned to the OH groups.

The absorption region is limited from both ends with the existence temperature range of the β phase and extends over the region from ~ 233 to 302,5°K. A decrease in temperature shifts the absorption maximum towards lower frequencies of the alternating electric field (Figure 5). The linearity of the lg $\nu_{\max} = f(1/T)$ relationship is, however, only approximately satisfied. The activation energy as estimated from the equation

$$\nu_{\max} = A \cdot e^{-\Delta H/RT}$$

is equal to 15 ± 2 kcal/mole. Below 260°K when the number of OH rotators rapidly falls down to zero, the activation energy becomes temperature dependent and ΔH increases.

The occurrence of dielectric absorption at MHz frequencies suggests a considerably higher internal friction of the OH groups in the TTBC molecules of phase β in comparison to 2,6 substituted and monomeric solid phenols whose τ is about 10^{-11}–10^{-12} sec and the activation energy is about 2 kcal/mole.

A sharp drop of ϵ'' at 302,5°K (Figure 5) where the molecular rotation becomes unfrozen may be explained as due to a stepwise reduction of the relaxation time for the free OH groups. As the studies on solutions show,[13] the absorption maximum will be then shifted to the GHz frequencies and the activation energy will drop down to the values which are characteristic of the free hydroxyl groups. Unfreezing of the molecular rotation in the plastic phase would simultaneously result in the occurrence of a new band whose relaxation time is about 10^{-8} sec.

Proton magnetic resonance spectra

The NMR studies have fully confirmed our previous conclusions based upon other measurement techniques and also supplied some new information concerning the dynamics of weakly polar methyl groups in the TTBC molecules.

The results are shown in Figures 6, 7 and 8. The NMR spectrum of TTBC exhibits two resonance signals which are close each to other and result from the protons of methyl and hydroxyl groups. The intensity ratio of the respective bands is 27:1. The chemical shift for hydroxyl protons is changed at 306°K from 1,13 ppm at infinite dilution in CCl$_4$ up to 1,28 ppm at the molar fraction equal to unity. On the other hand, for a pure compound a change from 1,32 ppm at 423°K (liquid) up to 1,57 ppm at 345°K (solid α phase) is obtained. If these small $\Delta\delta$ changes were attributed to weak association processes, then the calculated dimerization constant would be equal to 10^{-2} l.mole^{-1} [14]. TTBC may be then treated as a monomeric system.

Figure 6 shows the evolution of the proton signal for TTBC in the second type transition $\gamma \rightleftarrows \beta$ and in the first type transition $\beta \longrightarrow \alpha$. It is evident that the resonance line widths for methyl group protons are only slightly changed over the temperature range from 230 to 295°K. Instead, the resonance signal level for the hydroxyl protons is reduced either because of a gradual increase in line widths or because of a reduction in the number of independent OH rotators down to zero values at about 230°K.

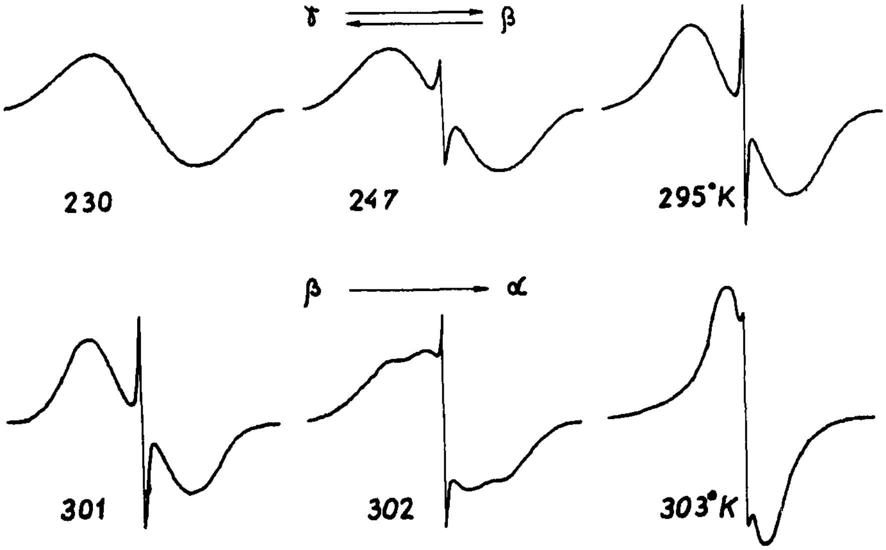

FIGURE 6 Evolution of the proton magnetic resonance signal in phase transitions $\gamma \rightleftarrows \beta$ and $\beta \to \alpha$.

Since, however, the dielectric studies at kHz frequencies show that simultaneously ϵ' tends to the value of ϵ'_∞, the second version stating that the rotator motion of the OH dipoles is frozen, should be accepted.

Fixing of the OH groups in the molecules does not, however, result in visible stepwise changes of proton signal widths for the methyl groups (Figure 8). Intermolecular and inner interactions between the adjacent methyl substituents are more essential in this case.

In the first type $\beta \longrightarrow \alpha$ transition (Figure 6) at 302,5°K the heights and widths of sharp hydroxyl proton signals remain unchanged while the resonance line width for methyl protons decreases stepwise from $\delta H = 2{,}35$Oe (phase β) to about 0,6 Oe (phase α).

Continued heating of alcohol (Figure 8) results in a decrease of the δH width below 0,1Oe in melted condition. A gradual decrease of temperature results in stronger intermolecular interactions and in an increase of internal friction of the substituents. This is reflected, above all, by the systematic broadening of the resonance signal of methyl protons until the molecular rotation $\alpha \longrightarrow \beta$ or $\alpha_m \longrightarrow \beta$ becomes frozen. Then a stepwise change of the resonance line width would take place. It is probable that the independent rotation motion of the t-butyl substituents as a whole becomes also frozen at that time.

A temperature drop over the range from 302,5°K to 180°K in the β and γ phase occurrence region does not result in visible δH changes. Only at 170°K the signal attributed to the frozen methyl group rotation becomes very strongly

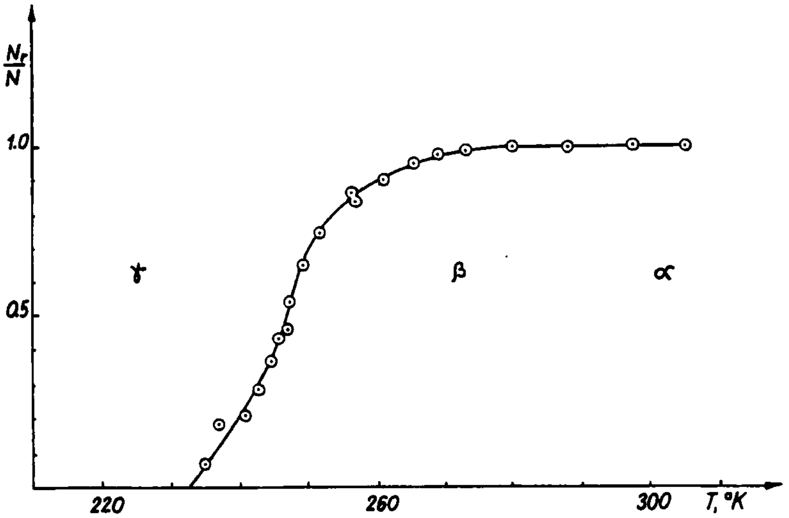

FIGURE 7 Temperature dependence of the fraction of rotating OH groups in solid TTBC

stepwise broadened. In effect, a doublet characteristic of CH_3 whose δH width is about 8 and 16Oe appears in the δ phase (below 170°K). The IR spectrum of the δ phase exhibits a single, narrow and symmetric band at 3608 cm^{-1} in the stretching frequency region of the OH groups.

The proton magnetic resonance method confirmed the existence of a temperature hysteresis for the $\alpha \rightleftarrows \beta$ transition (Figure 8). It is most essential that the interactions between the methyl protons in the rotation metastable α_m phase increase rapidly with decreasing temperature, almost approaching the state in which the alcohol molecules are fixed. This fact seems to justify the suggestion that freezing of rotation of the t-butyl substituents involves freezing of the molecular rotation. Both these motions would be then coupled each to other.

Since the proton signal level of OH groups in the $\alpha \rightleftarrows \beta$ phase transition remains unchanged, it may be suggested that all the OH dipoles have a sufficient

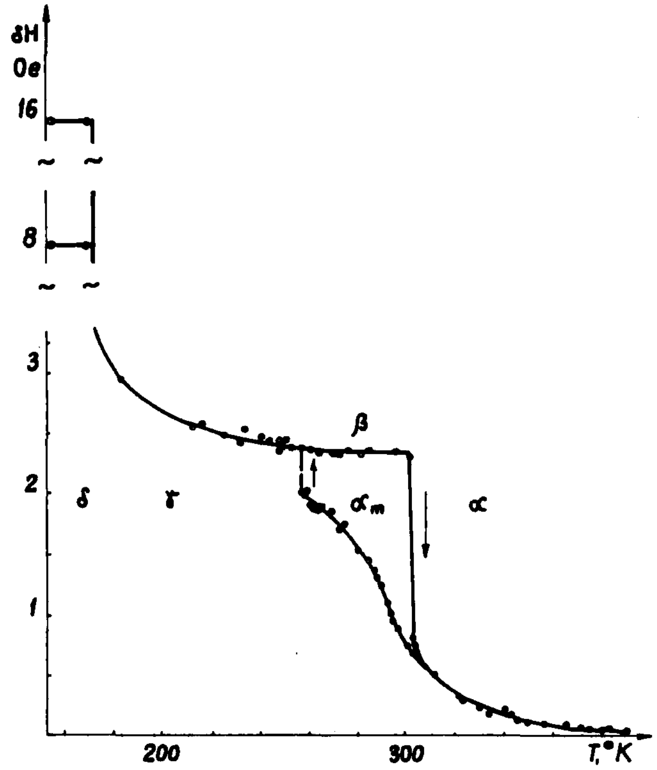

FIGURE 8 Effect of temperature on the proton magnetic resonance line width for methyl groups in TTBC

freedom of rotation (Figure 7). Attenuation of the signal would then be a measure of the number of frozen OH rotators. Using the relationship

$$\lg\left(\frac{N_r}{N}\right) = f\left(\frac{1}{T}\right)$$

it was possible to determine the potential barrier for rotation of the OH groups in the β phase.

The activation energy calculated by this method is 13 ± 1 kcal/mole. This result is close to that obtained from dielectric measurements.

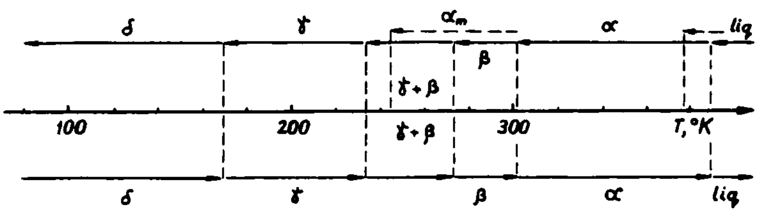

FIGURE 9 Temperature occurrence ranges of rotator inner and molecular phases:
α, (302,5 ± 0,5 — 391 ± 0,5 °K) – methyl, (t-butyl), hydroxyl groups rotation and molecular rotation
β, (270 ± 3 — 302,5 °K) – rotation of methyl and hydroxyl groups
β + γ, (233 ± 2 — 270 °K)
γ, (170 ± 3 — 233 °K) – rotation of methyl groups
δ, (80 — 170 °K) – frozen state.

CONCLUSIONS

Various measurments techniques enabled to discover a complex nature of dynamics in solid 2,2,4,4-tetramethyl-3-t-butylpentane-3-ol over an extensive temperature range from 90 to 400°K.

The results are shown in Figure 9. The potential barrier height for rotation of OH groups in the β phase is estimated at 13-15 kcal/mole. It is to point out, that there is no sharp transition point between β and γ forms.

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