مجلة جامعة بابل / العلوم الصرفة والتطبيقية / المجلد ١٠/ العدد ٣ : ٢٠٠٨

N.M.R STUDIES OF THE DYNAMICAL BEHAVIOUR OF METHYL GROUP IN SOME TERT-BUTYL SERIES.

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Abstract

The temperature dependence of nuclear (proton) spin lattice relaxation time, T_1. The tunnel splitting and the hopping rate depend upon the height and the shape of the hindering barrier to the methyl rotation and carry information on the group's molecular environment are reported for a number of samples containing tertiary – butyl groups.

The temperature rang was 4k to 300k. This date has been analyzed to provide estimates for the magnitudes of the three-fold potential barrier to reorientation of all methyl groups in these materials. At low temperature the motion of the tertiary-butyl protons can usually be neglected- cross relaxation due to the dipolar interaction, is much more rapid that spin – lattice relaxation. All protons of the sample relax as a single system.

In one or two cases tunneling is observed for the first time in tert – butyl. The T_1 results are used to evaluate tunnel frequencies in other cases. The results suggest the importance of collective motion of methyl groups in tert-butyl.

1- Introduction

The methyl group which is formed by three hydrogen atoms bonded to a single carbon atom, is one of the simplest and most common groups in organic chemistry. The intrinsic spin of the constituent protons makes the group accessible to study through techniques such as nuclear magnetic resonance and neutron scattering, giving both an ideal probe of the molecular environment and a test ground for theories of molecular motion.

The methyl group has been used as the ideal model system for study of atomic and molecules motion in the solid state. The resons for the choice have been discussed by a number of authorss as for example in the review by press and the references cited there in [1].

The tunneling rotation of the CH_3 is usually determined by the molecular environment of the group which sets up potential barriers to the rotation. Due to the symmetry of the group. The potential has at least 3-fold symmetry. Measurement of the CH_3 tunnel splitting at low temperature provide us with accurate values for the magnitude and shape of the potential barrier along with predictions for the hierarch of torsional state within the barrier. The dynamics behaviour of CH_3 can by studied and interpreted in terms of excitations and relaxation within the known ladder of energy level.

Despite the apparent simplicity of the system there has arisen a fundamental dichotomy of views regarding the theoretical description of the dynamical splitting or the reorientation rate. On the other hand the dynamics are described theoretically by invoking photon interaction explicity and one the other the role of the phonons is merely that a thermal bath to establish and maintain Boltzmann population within the torsional ladder of levels.

The latters has been approach of Clough et al (2,3). Here the phenomenological model of S., Steiskal and Gutowsky (4) has been modified and the quantum mechanical principle formalized to provide a single parameter theory in which the only variable is the barriers height. This is in contrast to theories which introduce.

Phonon interactions explicitly in which many unknown coupling are invoked (5). The materials chosen for this investigation are tert-butyl-nitrite, tert – butyl methylether, tert – butyl peroxid and pivalic acid (2,2,dimethyl propionic acid) are included here as examples of how the relaxation of $(CH_3)_3$ changes. It is our aim to find the behaviour of tertiary butyl group when it is in contact with different atoms. The comparision between the motional spectrum of different $(CH_3)_3$ materials will be related to the molecular structure.

In this work the temperature dependence of the nuclear (proton) spin lattice relaxation time (T_1) for all materials studied in order to provide a further test of the validity of Clough et al's model. The temperature dependence of T_1 is calculated (using only the measured tunnel splitting as in input parameter) and compared with experimental values. For selected materials the NMR technique was used to perform the experimental measurement. Nuclear magnetic resonance tunneling (NMR) is a powerful technique for the investigation of rotational tunneling of small molecules or molecular group like CH_3(1). NMR is sensitive to motion of proton spins through the dipole – dipole interaction.

2- Experimental Details:

Measurement of the CH_3 tunnel splitting using dipole – dipole driven NMR experiment, measurement of proton spin lattice relaxation T_1, were made on a pulsed N.M.R. spectrometer system which operates at 21 MHz. A saturation – recovery technique was employed and recovered magnetization was observed to grow exponentially within experimental error. All operation of N.M.R. spectrometer system were automated using LSI-11 minicomputer system. The sample which are liquid at room temperature were distilled and sealed under vacuum (10^{-3} Torr) in glass sample tube following repeated sequences of freeze – pump – thaw cycle to eliminate oxygen. The cryostate incorporated a solenoidal superconducting magnet and the sample temperature control within the variable temperature insert was better that 0.1 k throughout the temperature range.

In this work two pulsed N.M.R. spectrometers were used. A spin lock spectrometer operating at 26 MHz was used for the low field experiments. And the Bruker plused N.M.R spectrometer which operated at 21 MHz was used for T_1 experiments.

For T_1 experiments the temperature between room temperature and 4k could be reached by pumping helium from the bath surround the superconducting magnet into a dewar vessel running through its centeral bore. Aneedle valve controlled the flow rate.

A field cycling routine was employed as follows to scan the proton spin relaxation in the level crossing region. The magnetization was saturated with a burst of 90 pulses and the magnetic field then-switched immediately (0.3T per second) to an inspection field the region of interest where sample was relaxed for 30 sec. The field was then switched rapidly back to the spectometer operating field and the partially recovered magnetization measured with a 90 pulse repeated cycles incrementing the inspection field methodically at each step were made to trace out the tunneling spectra. The sample temperature was accurately maintained at atmospheric pressure.

A period of sample preparation at high magnetic field (Typically 5T) was made prior to each scan in the manner of the techniques described by Clough et al (6,7).

3- Results

3.1. T_1 versus temperature

in this section the results of the T_1 measurements will be presented and compared with the prediction of well established correlation between splliting of the ground torsional state (h,v_t) and temperature at which T_1 is a minimum and then well be connected to the molecular environment of methyl group in the unit cell.

Haupt (8) has modified the classical Bloembergam, Purcell, pound (Bpp) theory for nucler spin – lattice relaxation (9) to include the extra components in the spectral density function which related to the tunneling of CH_3.

Fig.(1). Fig(2), Fig(3) and Fig(4) display, the results of measurement upon the Tert – Butyl- nitrite, Tert- Butyl- methylether. Tert. Butyl peroxide, and 2,2 dimethy propionic acid respectively. Fig(1) shows the relaxation behaviour of tert – butyl nitrite, T_1 mimina is observed at 148.8K.

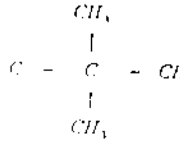
The low temperature minimum is associated with the measured tunnel frequency of $0.7 X 10^5$ Hz which corresponds to a three – fold barrier height of (2000k). The solid line represents fit using the reorientation rate calculated from methyl thermometer model using the calculated three – fold barrier height ([illegible]. Some simple organic samples which contain Tert – Butyl Group C- $(CH_3)_3$ such tert – butyl methylether, tert – butyl peroxid and pivalic acid are included here as examples of how the relaxation of $(CH_3)_3$ changes.

In spin lattice relaxation time versus temperature curve shown in Fig(2). We observe two minima. These are clearly observed at 74.7 and 148.8k. this is an interesting sample in its relaxation behaviour. In the temperature dependence of spin lattice relaxation T_1 the corresponding predicted barrier height for methyl groups is 1100 k we have predicted the tunnel splitting is $0.6 X 10^7$ Hz as we can see the tunnel splitting for second methyl group 2 is $0.5 X 10^5$ Hz corresponding to barrier height 2050 k. Fig(3) is a plot of T_1 versus the temperature inverse of tert – butyl peroxid, which shows the T_1 minimum at 163 k Fig(4) show the same story but for 2,2 dimethyl proplonic acid $(CH_3)_2CooH$ and it's minimum at 165k. Fig(5) shows the update correlation curve of different samples including the four samples mentioned above.

3.2. The low field measurement in tertary – Butyl Group sample.

Low field N.M.R. measurement of the tunnel splitting for the methyl group in tertiary butyl series supplied by Fulka chemical Ltd U.K. reveals that the methyl group tunnel splitting in the different energy range.

The molecular structure of tert – butyl has the form



$$C - \overset{CH_3}{\underset{CH_3}{C}} - CH_3$$

The low field NMR data for this series are shown from Figures 6-8. Each one is a plot of magnetic field in mT versus the magnetization in arbitrary units. A summary of the tunneling frequency of these samples is shown in table [1]. From it one can see the barrier height and tunnel frequency changes. These changes in the barrier heights and the tunnel frequencies are presumed to be due to the difference in the crystal field for different sample.

Six typical sets of results for pivalic acid are shown in fig (6) a,b for irradiation frequencies of 500 MHz, 550 MHz, 600 Mhz, 700 MHz, 800 Mhz and 850 MHz. They all show a clear Δm=1 transition near 14 mT. This transition occurs at field given by $B=\omega/2\pi$ [11] with a side band at lower field. As expected the main feature moves towards higher field as the irradiation frequency is increased with the sideband displacement remaining constant. The upper sideband is very weak at these frequencies as noted by clough et al.

This is thought to be due to level crossing in the energy level diagram occurring at 8mT [12]. At other irradiation frequencies the upper sideband may be more intense that the lower one, or both may have similar intensities. The $\Delta m=2$ spectrum can be seen centered at ~8mT. this transition occurs at field given by $B= \omega /2\gamma$ [13] where ω is the applied irradiation frequency, and also shows clear sidebands. The tunner frequencies have been measured and are found to be equal to (382±5), (112±5) and (90±5) KHz.

Tert-butyl peroxide has the molecular formula $(CH_3)_3cooc(CH_3)_3$. The data for tert – butyl peroxide is very similar to that for pivalic acid (2,2 dimethyl propionic acid). A typical example is shown in Fig.(7) for an irradiation frequency of 500 KHz. The Δm-1 and $\Delta m=2$ transitions can easily be seen. We can see two tunnel frequencies lie at (170±2) and (127±2) KHz in Fig(8). Similar shoulders are seen on the $\Delta m=1$ peak at other irradiation frequencies. These vary in intensity in a similar way to those seen in pivalic acid.

4- Discussion of T_1 Results

In Fig(2) the proton relaxation time T_1 exhibits two minima at [illegible]8-8k and 74.8k. The first can be confidently assigned to the effect of methyl group rotation within the tert iray butyl groups. This motion is [illegible] strongly hindered [illegible] indicated by the relatively high temperature at which the T_1 minimum occurs. T[illegible]ng plays no significant role at this temperature and the (BPP) theory [illegible] adequately for this high temperature region. The T_1 at the minimum in fig (2) is small enough to indicate that almost all the protons in the sample are involved in the motion. In [illegible] samples a low temperature minimum occurs due to a more weakly hindered methyl group. The data of fig.(2) is remarkable because the t-butyl minimum [illegible] very shallow. The only possible explanation for this is that the t-butyl group already rotates as a whole at low temperatures. Thereby contributing to the low temperature minimum when methyl groups begin to rotate within the t-butyl group the dipole-dipole interactions are already time dependent due to the rotation of the t-butyl group as a whole. Cross relaxation due to the dipolar interactions is still much more rapid than [illegible] – lattice relaxation [14]. Consequently all protons of the sample relax [illegible] a single [illegible]m. If all protons of a single molecule are relaxed by a [illegible] methyl group, the [illegible]ation is slower than if the group were isolated [illegible] and fig [illegible] the low temperature minimum of fig(2) is deeper than it would be if it were due [illegible] methyl group only, thus confirming the rotation of t-butyl [illegible] a mechanism.

5- Conclusion

In this work measurement of the temperature dependence (T) of the protons spin – lattice relaxation rate (T_1) in the t-butyl [illegible] ether [illegible] – butyl [illegible] t-butyl peroxide, 2,2 dimethyl proplonic acid, at a [illegible] frequency [illegible] $\omega/2\pi =$ [illegible].

The relaxation is caused by the modulation of the proton [illegible] dipole interaction by the reorientation of the t-butyl group $[C(CH_3)_3]$ and [illegible] three constituent methl group (CH_3). It is necessary to account [illegible] the fact [illegible] methyl reorientation is superimposed on the rotation of the whole group. These [illegible] aid in the investigation of the nature of molecular reorientation. [illegible] have [illegible] report our experimental work in these sample to point [illegible] a few interesting [illegible] important features of the general problem of the nuclear [illegible] – lattice relaxation [illegible] molecular solids as the temperature is varied.

The general theory of spin – lattice relaxation due to methyl rotation applies equally well to the t-butyl group. The temper[illegible] f the T$_1$ [illegible] minima [illegible] similar to other CH$_3$ group attached to Sp^3 hybridised a[illegible]. The va[illegible] of T$_1$ at [illegible] minimum shows that in most cases rotation is fast compa[illegible] with ro[illegible] n of the [illegible] le t-butyl group, but the case of t-butyl methyl e[illegible] is anom[illegible] us. The [illegible] mperature dependences of proton spin –lattice relaxation [illegible] from 5[illegible] 5k is re[illegible] l for two samples containing t-butyl group whose tun[illegible] frequen[illegible] have [illegible] measured very precisely during this work. They are te[illegible] butyl p[illegible] de and [illegible] dimethyl prpionic acid. This is the first time that [illegible] motio[illegible] been [illegible] red in t-butyl groups.

We interpret the T$_1$ minimum versus te[illegible] ture de[illegible] with the t[illegible] y, Clough et al. this is used to estimate the t[illegible] for the [illegible] butyl se[illegible] and other samples. The dominant fact emerg[illegible] fro[illegible] is study [illegible] that [illegible] l has a characteristic temperature of T$_1$ mi[illegible] ([illegible]). All compounds [illegible] rate this results. We attribute this to the in[illegible] methyl [illegible] ation a[illegible] ng the t-butyl group as a whole is not ro[illegible] is temp[illegible]. T[illegible] $_3$ tunnel frequency is expected to be about 10[illegible] KH[illegible] an[illegible] measure[illegible] conf[illegible] is. These are the first measurement of the [illegible] tunnel[illegible] in t-bu[illegible] roups. [illegible] coupling between the group is expected to b[illegible] l evide[illegible] this [illegible] complex nature of the tunneling spectrum.

A small number of sample[illegible] T$_1$ min[illegible] below [illegible] and we attribute this to other methyl groups [illegible] ering b[illegible] nd to [illegible] tation of the whole group. This is confirmed [illegible] of a [illegible] mini[illegible] at 165 K. the tunneling splitting for the t-bu[illegible] ilar to [illegible] obtained [illegible] dipole – dipole driven nuclear resonance exp[illegible] for [illegible] etone [illegible].

References

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الخلاصة

تناول [illegible] البحث [illegible] الحرارية [illegible] من خمول شبكة البروتون النووي (T_1). وبين بأن الخرق لحاجز الجهد [illegible] معدل [illegible] على [illegible] وشكل [illegible] جهد الاعاقة لدوران المثيل وهذه المعلومات حددت لعدد [illegible] النماذج [illegible] لي مجموعة [illegible] بروتايل [illegible].

مدى [illegible] الحرارة [illegible] كان من [illegible] ٣٠٠ كلفن [illegible] البيانات حللت لكي تحدد التقديرات لمحصلة حاجز الجهد [illegible] الطيا [illegible] يتحكم بحركة مجموعة [illegible] هذه المواد.

عند [illegible] الحرارة [illegible] حركة [illegible] بروتونات [illegible] الثلاثي غالباً ما تهمل وتكون حالة تقاطع الخمول [illegible] هو [illegible] من خمول [illegible] البرمي. جميع بروتونات العينة يحصل خمولها [illegible] لذا [illegible] من [illegible] لوحظت [illegible] في البروتايل الثلاثي.

وهنا [illegible] برزت [illegible] الحركة [illegible] لمجموعة [illegible] في البروتايل الثلاثي ((أي خمول مجموعة المثيل الثلاثي [illegible])).

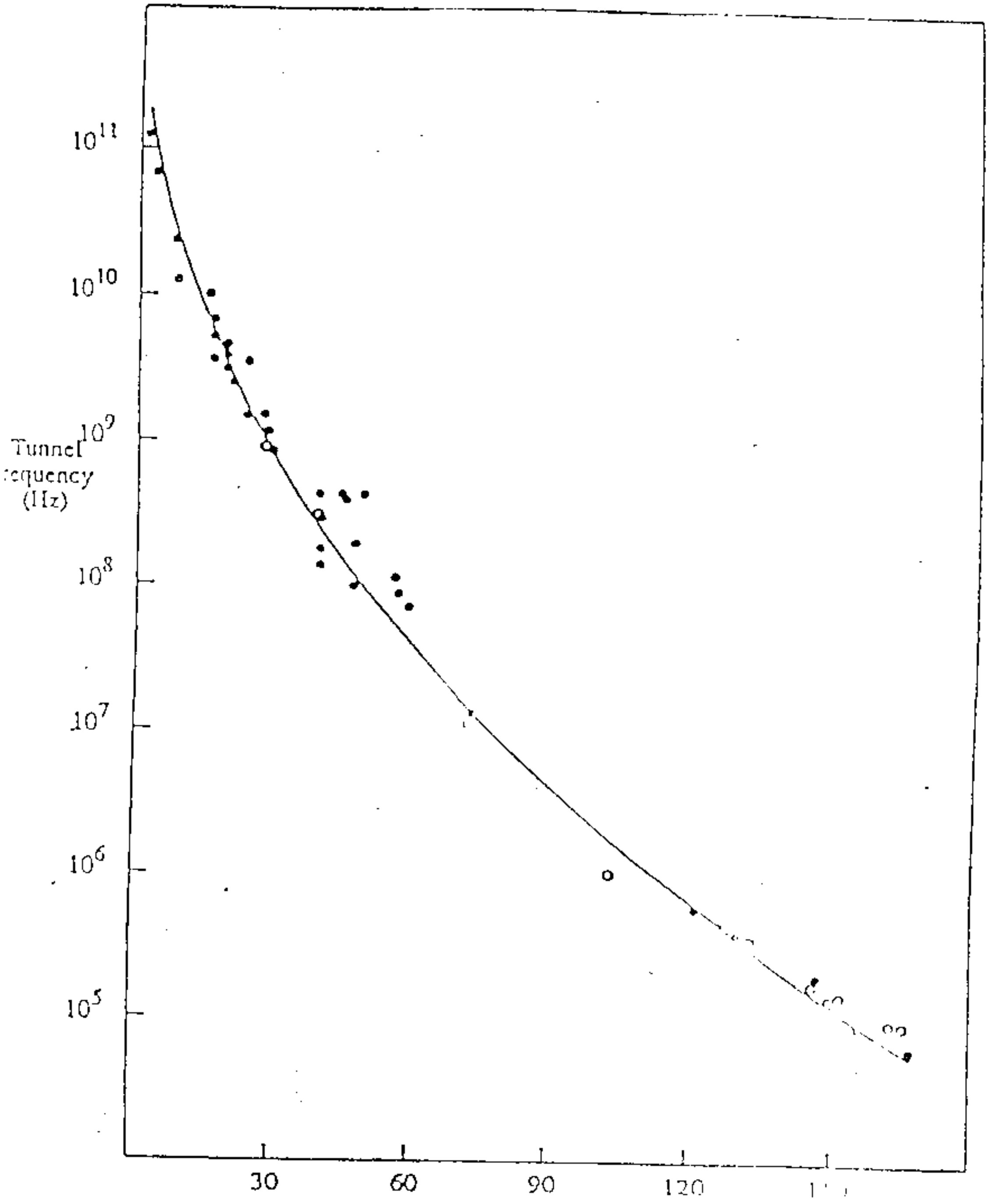


Fig. 2

The correlation between the tunneling frequency and the temperature at which T1 is a minimum for a methyl group. The open circles represent the new experimental measurements.

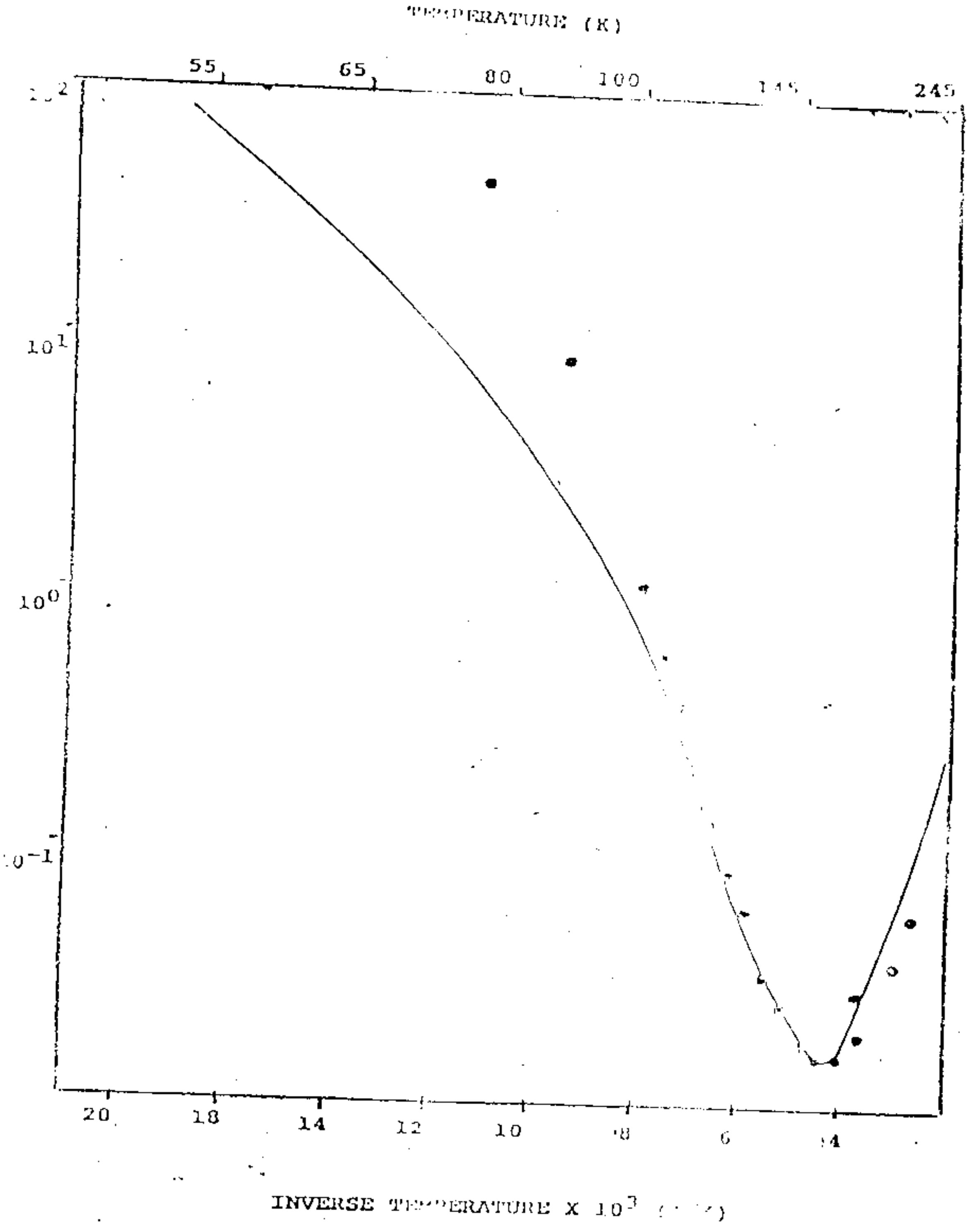


Fig. 3

The temperature dependence of T1 in tert-butyl peroxide at NMR frequency 21 MHz.

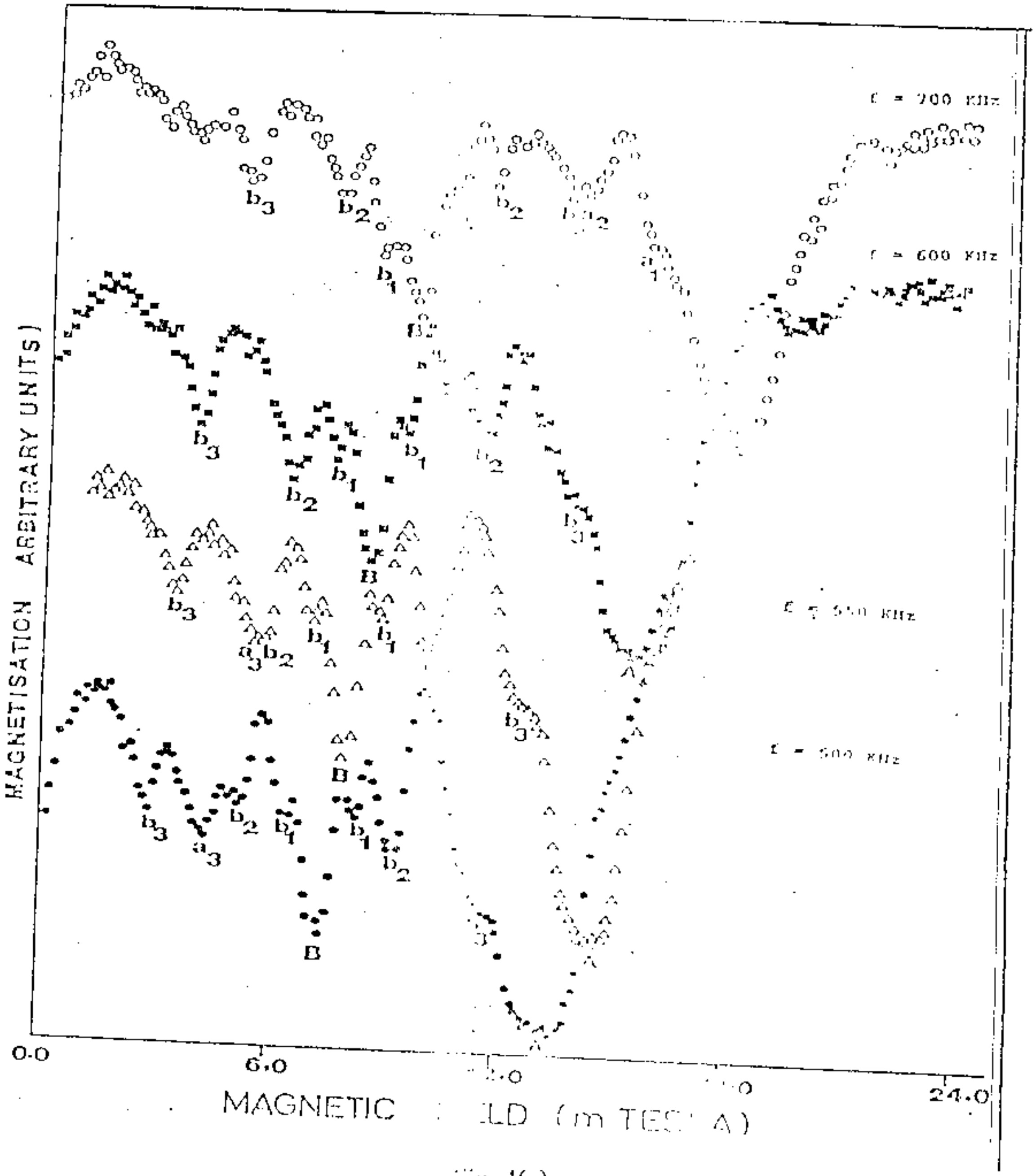
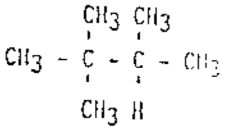
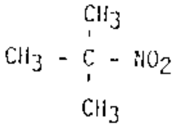
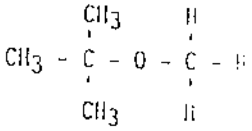
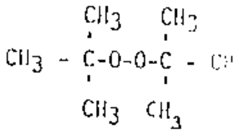
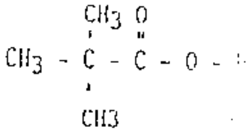


Fig. 4(a)

The low field NMR spectra (4k) of pivalic acid (2,2 dimethyl propionic acid recoded at a variety of frequency.

2,2,3 Trimethyl Butane	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3$	114.3	1×10^{6}		1600	1240
Tert-butyl nitrite	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-NO_2$	146.8	0.7×10^{5}		2000	1180
Tert-butyl methylether	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-\underset{H}{\overset{H}{C}}-H$	74.7 148.8	0.6×10^{4} 0.5×10^{5}		1100 2050	577 1211
Tert-butyl peroxide	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	163	8×10^{4}	[illegible] 2 [illegible] 2	1850	770
Pivalic Acid	 $CH_3-\underset{CH3}{\overset{CH_3}{C}}-\overset{O}{C}-O-H$	165	8×10^{5}	[illegible] 5 [illegible] 5 [illegible] 5	1700	480

T [illegible] 1

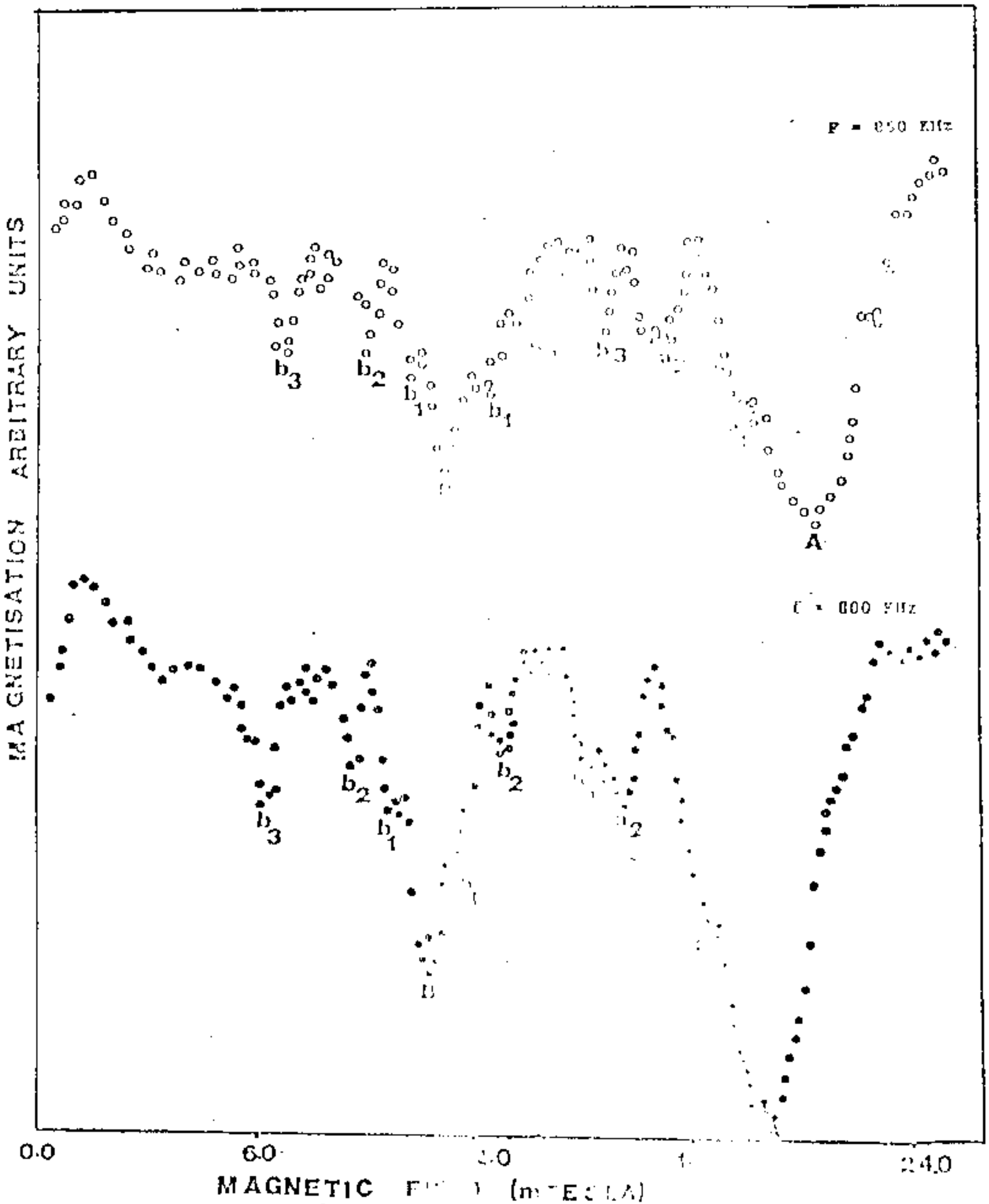


FIG 5·9b

Fig. 4(b)

The low field NMR spectra (4k) of pivalic acid (2,2 dimethyl propionic acid recoded at a variety of frequency.

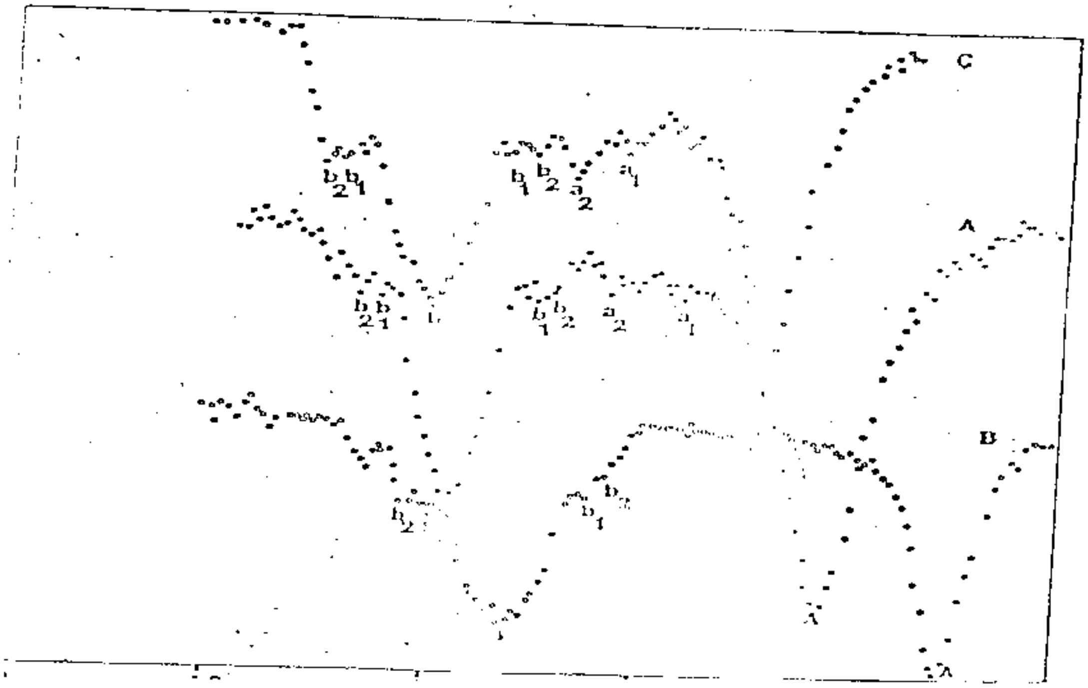


Fig. 5

The low field NMR spectra (1k) of tert-butyl peroxide
Recorded at a veriety of frequencies
A.Tert-Butyl peroxide (RF=500 [illegible]
B.Tert-Butyl peroxide (RF [illegible]
C.Text-Butyl peroxide (RF=4700

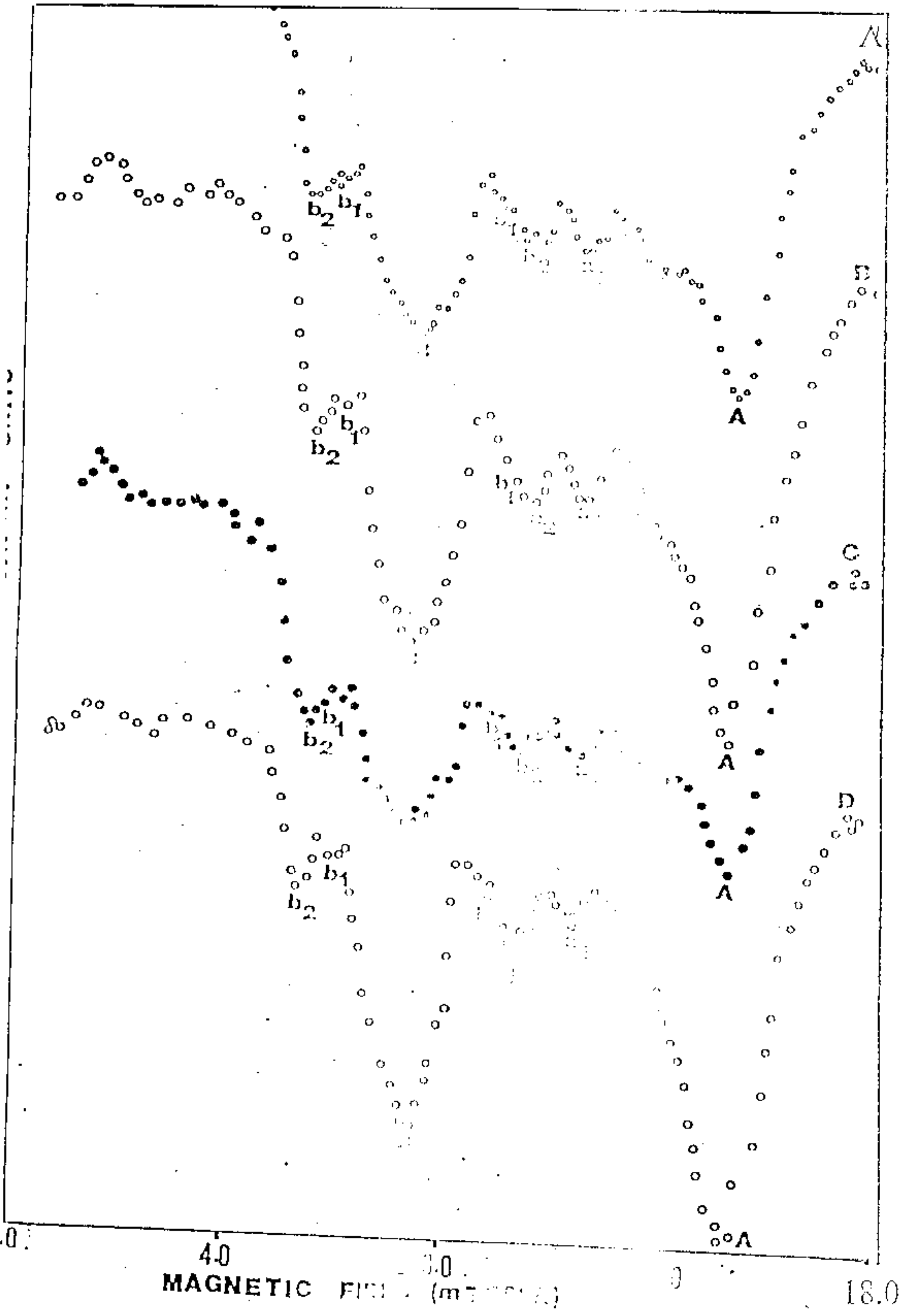


Fig6

The low field NMR spectra (4k) of tert-butyl peroxide.

A.Tert-Butyl Peroxide (RF [illegible]

B.Tert-Butyl Peroxide (RF [illegible]

C.Text-Butyl Peroxide (RF [illegible]

D.Text-Butyl Peroxide (RF [illegible]