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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

THE RADIOLYTIC AND PYROLYTIC DECOMPOSITION OF ORGANIC COOLANTS

III. THE RADIOLYSIS AND PYROLYSIS OF m-TERPHENYL AND m-TERPHENYL-d_{14}

by

G. JUPPE, H. RAU and F. DORPEMA

1967

ORGEL Program
Joint Nuclear Research Center
Ispra Establishment - Italy
Chemistry Department
Organic Chemistry

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quaterphenyls, triphenylbenzenes and triphenyl, and high boilers were formed with the deuterated compound. The reaction orders for the decomposition of the starting terphenyls as well as for the formation of the reaction products were determined. The quantitative differences in the reaction rates and the composition of the pyrolysis products are attributed to a small difference in the bond dissociation energy between the aromatic CH- and CD-bonds, which leads to a primary isotope effect in the homolytic rupture of these bonds.

The radiolysis of unlabelled m-terphenyl and m-terphenyl-d_{14} by 2 MeV electrons also showed a greater stability of the deuterated terphenyl. A lower rate of m-terphenyl-d_{14} destruction was observed. The formation of quinqua + hexaphenyls and highboilers was also found lower for the labelled compound. The reaction mechanism of the radiolytic decomposition of aromatic hydrocarbons is discussed.

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I. G. Juppe, M. Alvarenga and H. Hannaert ; The Pyrolytic Decomposition of Terphenyls ; EURATOM Report EUR 1647.e (1964).

II. G. Juppe, G. Wedekind, H. Rau and G. Schütz ; The Postpyrolysis of Preirradiated OM2 ; EURATOM Report EUR 3287.e (1967).

V. G. Juppe and H. Rau ; The Thermal Decomposition of o-, m- and p-Terphenyl in the Presence of Attapulgus Clay ; EURATOM Report EUR 3281.e (1967).

VII. G. Juppe and H. Rau ; The Pyrolysis of High Boiling Residue ; EURATOM Report EUR 3158.e (1966).

SUMMARY

We have investigated both the radiolysis and the pyrolysis of unlabelled m-terphenyl and m-terphenyl-d_{14}. A comparison of the kinetics of pyrolysis showed that the deuterated compound suffered lower destruction of the starting material than did the m-terphenyl. Furthermore less hydrogen and aliphatic hydrocarbons, benzene, diphenyl, quaterphenyls, triphenylbenzenes and triphenyl, and high boilers were formed with the deuterated compound. The reaction orders for the decomposition of the starting terphenyls as well as for the formation of the reaction products were determined. The quantitative differences in the reaction rates and the composition of the pyrolysis products are attributed to a small difference in the bond dissociation energy between the aromatic CH- and CD-bonds, which leads to a primary isotope effect in the homolytic rupture of these bonds.

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Theoretically three different approaches could be considered which might lead to an increase in the stability of an ORGEL coolant under radiolytic and pyrolytic conditions:

a) Inhibitors could be added being effective in suppressing consecutive or chain reactions following the initially appearing bond ruptures by pyrolysis and probably also radiolysis. These scavengers would disappear during the decomposition processes.

b) Energy transfer agents, being initially added to the coolant, could provide means for dissipation of the excitation energy delivered by the high energy radiation prior to the decomposition of the irradiated molecules. A decrease in the radiation induced decomposition of the coolant would result. The additive acting like an energy sponge would not be used by chemical intermediates being formed by the radiolysis of the coolant molecules.

c) Compounds could be found which are more stable towards high energy radiation and heat than di- or terphenyls.

Out of the last two of the above mentioned reasons deuterated terphenyls, alone or in mixture with unlabelled material, should have better pyrolytic and radiolytic properties than hydrogen containing terphenyls:

In deuterated aromatic molecules the zero point energy of the C-D-vibrations is lower than that of C-H. The stronger C-D-bond is expected to be more resistant towards the degrading action of both radiation and heat. A higher temperature for the organic reactor operation could be chosen giving the same decomposition rates as with unlabelled material. Besides the improvement of the efficiency for the thermal process, the neutron economy would also profit from the use of deuterated material: the cross section for thermal neutrons by deuterium is approximately 6oo times smaller than that of hydrogen.

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In a mixture of deuterated and unlabelled terphenyls energy transfer could be expected, leading to a possible decrease of the decomposition induced by high energy radiation. It has been shown that in a mixture of benzene and deuterobenzene both agents protect each other to a certain extent against radiation damage1). Both the hydrogen and the acetylene yields were found to be smaller than had been expected from the yields from the pure substances. The production of acetylene was even less than from either component irradiated separately.

In order to decide on these questions and to evaluate the possible use of deuterated terphenyls as reactor coolants from the radiation and high temperature chemistry point of view we studied the thermal and radiation induced decomposition of m-terphenyl and m-terphenyl-d_{14} and compared the kinetics of the radio- and pyrolysis.

1 - INTRODUCTION

The radiation chemistry of deuterated aromatic compounds has received a great deal of attention during recent years. The large difference of ca. 1,2 kcal/mole in zero point energy between C-D- and C-H-vibrations1) and the strong isotope effect for the rupture of aromatic C-D-bonds2) opened possibilities for deciding many mechanistic questions on the radiolytic decomposition of the most simple aromatic system, benzene1,3). Only one third of the hydrogen yield and two thirds of the acetylene yield were observed when irradiating deutero-benzene instead of the unlabelled material with 1,5 MV electrons 1). The G-values for total hydrogen formation did not show a proportional increase with increasing deutero-benzene concentrations but showed the characteristics of a "eutecticum". The irradiation of a 20% deutero-benzene mixture yielded even less acetylene than pure C_6D_6. The results were explained with a mutual protection mechanism, the deuterated and unlabelled benzene acting to provide for each other more effective and highly competitive processes by which energy can be transferred and dissipated before decomposition of the molecules has a chance to occur.

This intermolecular mutual protection between two different molecule species is not effective under inner molecular conditions: J.G. Burr and co-workers 4) investigated the radiolytic decomposition of partly and totally deuterated biphenyls. The overall gas production under identical irradiation conditions was found to decrease in a linear relationship with increasing deuterium content. No difference for the $G_{(gas)}$-value for deuterium in different molecular positions was observed.

In a Canadian patent M.M. Wright 5) suggested the use of diphenyl-d_{10} as an improved reactor coolant due to its higher stability towards radiation and its better neutron economy. J.M. Rayroux and P. Baertschi 6) reinvestigated the thermal and radiation behavior of totally deuterated diphenyl more recently. The labelled material yielded only half of the total gas measured for unlabelled diphenyl during in-pile radiolysis and pyrolysis at 460°. The yields for terphenyls and higher boiling compounds were found to be 38% lower when using deuterobiphenyl.

2 - MATERIALS AND METHODS

2.1 - MATERIALS

m-Terphenyl[7)] was purified by distillation, from traces of p-terphenyl and then recrystallized from petrolether until gaschromatographic purity had been achieved. m-Terphenyl-d_{14} had been synthesized by H/D-exchange of m-terphenyl[8)]: The isotopic purity of 96% was determined by mass-spectroscopy.

2.2 - PYROLYSIS

The preparation and the pyrolysis of the samples were carried out as previously described[9)]. The samples of m-terphenyl and m-terphenyl-d_{14} were pyrolyzed in pairs, both containing 2,o g of material. The chosen temperatures of 425°C and 441°C were measured continuously by thermoresistance and did not fluctuate more than ± 1°C around the set point.

2.3 - RADIOLYSIS

5o ± 1 g of either labelled or unlabelled material were degassed by repeated melting and freezing under a high vacuum, and filled under argon into the stainless steel irradiation vessels previously described[1o)]. The initial temperature of 96°C, maintained by the constant temperature water in the heating mantle of the vessel, rose during irradiation to 12o ± 1°C and was kept constant at this value by the temperature control system described before[1o]. During the 9 hour runs irradiating with 1,5 MV/2oo uA electrons six samples of o,46 to o,72 g were taken at 9o minute intervals. The total dose absorbed was finally $9,4 \cdot 1o^9$ rads. The speed of the internal magnetic stirrer was 12oo rpm. which was calculated from the signals observed on an oscilloscope screen. These were formed by the induction of a small current in a coil on the outer side of the irradiation vessel, by a small permanent magnet fixed to the rotating propeller inside the vessel.

2.4 - ANALYSIS

The analyses for total gas, hydrogen, methane, ethane, ethylene, acetylene, propane, propene, n-butane, i-butane, 1-butene, 2-butene, n-pentane, and i-pentane from the pyrolysis experiments were carried out as previously described[11]. The hydrocarbons resulting from the pyrolysis of m-terphenyl-d_{14} could not be analyzed because no test mixtures for the determination of the cracking pattern of mass spectroscopy were available. The analyses for benzene, diphenyl, the terphenyls, the quaterphenyls and the high boilers have also been described before[12].

3 - RESULTS

3.1 - PYROLYSIS

3.1.1 - FORMATION OF GASES

A comparison of the total gas formation during the pyrolysis of m-terphenyl and m-terphenyl-d_{14} at 425°C is given in fig. 1.

3.1.2 - FORMATION OF LIQUIDS

A comparison of the experimental data concerning the formation of benzene and diphenyl from m-terphenyl and m-terphenyl-d_{14} is illustrated in fig. 2 to 3.

The rates for the observed m-terphenyl decrease during thermal decomposition at 425°C and 441°C of the two m-terphenyls are listed in fig. 4.

The corresponding kinetics of the formation of o,m-quaterphenyl, o,p-quaterphenyl and 1,2,4-triphenylbenzene, m,m-quaterphenyl and 1,3,5-triphenylbenzene, m,p-quaterphenyl, p,p-quaterphenyl and triphenylene and the sum of all quaterphenyls and triphenylene and triphenylbenzenes are compared in fig. 5 to 1o.

The rates for the formation of high boilers during the thermal decomposition of m-terphenyl and m-terphenyl-d_{14} are listed in fig. 11.

On the basis of a zero order reaction for the formation of benzene and diphenyl during the pyrolysis of m-terphenyl and m-terphenyl-d_{14} at 425°C and 441°C the following approximate rate constants listed in table 1 have been calculated:

TABLE 1 - RATE CONSTANTS OF ZERO ORDER REACTIONS (10^{-4}mole·$l^{-1}h^{-1}$)

	425°C		441°C	
	m-TERPHENYL	m-TERPHENYL-d_{14}	m-TERPHENYL	m-TERPHENYL-d_{14}
BENZENE	1,15	0,9	9,0	7,2
DIPHENYL	1,35	0,8	4,7	2,7

On the basis of a first order reaction for the formation of p,p-quaterphenyl and triphenylene, o,m-quaterphenyl, o,p-quaterphenyl and 1,2,4-triphenylbenzene, m,m-quaterphenyl and 1,3,5-triphenylbenzene, m,p-quaterphenyl, the sum of all quaterphenyls and high boilers and the decrease in starting m-terphenyl the approximate initial rate constants listed in table 2 have been calculated:

TABLE 2 - PYROLYSIS: RATE CONSTANTS OF FIRST ORDER REACTIONS ($mg/g\ h^{-1}10^{-2}$)

	425°C		441°C	
	m-TERPH.	m-TERPH.-d_{14}	m-TERPH.	m-TERPH.-d_{14}
m-TERPHENYL	34	28	175	130
p,p-QUATERPHENYL[a)]	-	-	2,3	1,5
o,m-QUATERPHENYL	0,6	0,35	2,0	1,2
o,p-QUATERPHENYL[b)]	0,2	0,15	1,2	0,7
m,m-QUATERPHENYL[c)]	5,5	4,0	19	13
m,p-QUATERPHENYL	4	3	11	8
SUM QUATERPHENYLS[d)]	10	8	33	22
HIGH BOILERS	27	21	110	85

a) including triphenylene
b) including 1,2,4-triphenylbenzene
c) including 1,3,5-triphenylbenzene
d) including triphenylene, 1,2,4- and 1,3,5-triphenylbenzene

Table 3 shows the composition of the liquid products after 2oo hours pyrolysis at 425°C and 441°C:

TABLE 3 - PYROLYSIS: COMPOSITION OF LIQUIDS (wt %)

	425°C		441°C	
	m-TERPH.	m-TERPH.-d_{14}	m-TERPH.	m-TERPH.-d_{14}
BENZENE	0,70	0,55	2,8	2,2
DIPHENYL	1,7	1,1	5,8	3,6
m-TERPHENYL	93,2	94,5	70,5	76
p,p-QUATERPHENYL[a)]	-	-	0,23	0,15
o,m-QUATERPHENYL	0,12	0,07	0,40	0,24
o,p-QUATERPHENYL[b)]	0,04	0,03	0,23	0,14
m,m-QUATERPHENYL[c)]	1,2	0,8	3,7	2,6
m,p-QUATERPHENYL	0,8	0,6	2,2	1,6
SUM QUATERPHENYLS[d)]	2,05	1,65	6,7	4,4
HIGH BOILERS	5,4	4,2	22	18,6

a) including triphenylene
b) including 1,2,4-triphenylbenzene
c) including 1,3,5-triphenylbenzene
d) including triphenylene, 1,2,4- and 1,3,5-triphenylbenzene

3.2 - RADIOLYSIS

The rates for the observed m-terphenyl decrease during the radiolytic decomposition of m-terphenyl and m-terphenyl-d_{14} are listed in fig. 12.

The kinetics of the formation of quinqua- and hexaphenyls (with the exception of p,p-hexaphenyl), originating from the radiolysis of unlabelled and labelled m-terphenyl are compared in fig. 13. The kinetics of the formation of high high boilers, i.e. p,p-hexaphenyl and higher polymers are shown in fig. 14.

Only traces of benzene, diphenyl and quaterphenyls were found in both reaction mixtures after the radiolysis.

Table 4 shows the composition of the liquid products after 9,5 • 10^9 rads absorption:

TABLE 4 - RADIOLYSIS: COMPOSITION OF LIQUIDS (wt %)

	m-TERPHENYL	m-TERPHENYL-d_{14}
m-TERPHENYL	70,8	87,4
QUINQUA- AND HEXAPHENYLS[a)]	6,6	2,25
HIGH HIGH BOILERS	22,6	11,35

a) without p,p-hexaphenyl

4 - DISCUSSION

4.1 - EFFECT OF PYROLYSIS

4.1.1 - FORMATION OF GASES

A comparison of the formation of gases originating from the pyrolysis of m-terphenyl and m-terphenyl-d_{14} shows the following:

The total gas formation can in both cases be described as a zero order reaction. 55% less gas is obtained from the totally deuterated material.

4.1.2 - FORMATION OF LIQUIDS

4.1.2.1 - FORMATION OF BENZENE AND DIPHENYL

The formation of benzene and diphenyl from both terphenyls can be described as resulting from a zero order reaction. 22% less benzene and 38% less diphenyl is formed from the deuterated compound at both 425°C and 441°C.

4.1.2.2 - m-TERPHENYL DECREASE

The disappearance of the initial m-terphenyl can both for the labelled and the unlabelled material be described as resulting from a first order reaction. 2o% less deuterated terphenyl than unlabelled m-terphenyl is decomposed at both 425°C and 441°C.

6o kcal/mole are calculated as approximate activation energies for the decrease in starting material when pyrolyzing the hydrogen containing aromatic hydrocarbon. The activation energy for the decrease of totally deuterated m-terphenyl was determined to be app. 61 kcal/mole. These values could not be determined with high precision, due to the choice of only two temperatures for our kinetics. They, nevertheless, lie well beyond the bond dissociation energies for an aromatic CH-, CD- or CC-bond.

4.1.2.3 - QUATERPHENYL FORMATION

A major portion of the products of the pyrolysis of both unlabelled and deuterated m-terphenyl consists of quaterphenyls, triphenylbenzenes and triphenylene. The formation of the sum of these C_{24}-compounds can in both cases be described as resulting from a first order reaction.

3o% less quaterphenyls, triphenylbenzenes and triphenylene are formed from deutero-terphenyl than from unlabelled terphenyl at 425°C; 34% less at 441°C.

Additional information is obtained from the analyses for the individual compounds: 4o% less o,m-quaterphenyl and 1,2,3-triphenylbenzene, 35% less o,p-quaterphenyl and 1,2,4-triphenylbenzene, 35% less p,p-quaterphenyl and triphenylene, 3o% less m,m-quaterphenyl and 27% less m,p-quaterphenyl are formed when pyrolyzing the labelled m-terphenyl instead of the unlabelled compound. The composition of the quaterphenyl fractions are in both cases approximately the same: when pyrolyzing labelled material at 441°C the main products are m,m-quaterphenyl and 1,3,5-triphenylbenzene (16 parts), followed by m,p-quaterphenyl (1o parts), o,m-quaterphenyl (2parts), o,p-quaterphenyl and 1,2,4-triphenylbenzene (1 part) and p,p-quaterphenyl (1 part). Also from unlabelled m-terphenyl the main products are m,m-quaterphenyl and 1,3,5-triphenylbenzene (19 parts), followed by m,p-quaterphenyl (12 parts), o,m-quaterphenyl (2 parts), o,p-quaterphenyl and 1,2,4-triphenylbenzene (1 part) and, finally, p,p-quaterphenyl (1 part). Similar data are also obtained at 425°C.

4.1.2.4 - HIGH BOILER FORMATION

The formation of high boilers from the pyrolysis of both m-terphenyl and m-terphenyl-d_{14} can be described as resulting from a first order reaction. 22% less high boilers are formed from the deuterated starting material at 425°C, 20% less at 441°C. Regardless of whether deuterated or unlabelled starting material was used, the high boiler fraction contained in both cases app. 38% quaterphenyls, triphenylbenzenes and triphenylene.

4.2 - REACTION MECHANISM OF THE PYROLYSIS OF DEUTERATED TERPHENYLS

The observations which led to the proposal of a reaction mechanism for the pyrolytic decomposition of unlabelled terphenyls 13) apply equally well to the thermal decomposition of totally deuterated terphenyls:

a) The activation energy found for the over all disappearance of m-terphenyl-d_{14} during the pyrolysis is considerably smaller than the bond strength of the CC-bond between the two aromatic rings or the bond dissociation energy of an aromatic CD-bond.

b) The decomposition reaction can be described as a first order reaction at lower conversion rates.

c) The formation of benzene and diphenyl appears in an approximate 1 : 1 molar ratio.

d) There is evidence for a higher molar formation of quaterphenyls than quinquaphenyls.

These observations are in agreement with a radical reaction mechanism as outlined in fig. 14. As initial reaction steps CC- or CD-bond ruptures appear, giving rise to the formation of deuterium-, phenyl-, diphenyl-, and terphenyl radicals. Subsequently a system of consecutive reactions can be devised in which for each stable molecule of end product (deuterium, benzene, diphenyl, terphenyls, quaterphenyls, quinquaphenyls, hexaphenyls) one new radical appears (deuterium-, phenyl-, diphenyl-, terphenyl-, quaterphenyl-, quinquaphenyl-, and hexaphenyl radicals). The pseudo chain terminates by dimerisations which are considered to have no activation energy. This process would be analogous to the Rice-Herzfeld mechanism for the thermal decomposition of aliphatic hydrocarbons.

The quantitative differences between the pyrolysis of unlabelled and deutero-terphenyl concerning the decomposition rates and the rates for the formation of reaction products always point in the same direction of lower decompositions and less product formations from the totally deuterated terphenyl. The compositions of the reaction products remain approximately the same.

These observations can be partly explained by the difference in the bond dissociation energies of app. 1,2 kcal/mole[14] between an aromatic CH- and CD-bond. The initial rupture of a CD-bond resulting in the formation of a deuterium and a terphenyl radical would require a somewhat higher temperature for yielding the same primary rate constant of CH-ruptures occurring during the pyrolysis of unlabelled terphenyl at a certain lower temperature.

This statement is consistent with our observation that for the pyrolysis of m-terphenyl-d_{14}, temperatures 5 - 7°C higher are required in order to achieve the same rates of decomposition and the same rates of product formation as during the thermal decomposition of unlabelled m-terphenyl.

The quantitative influence of primary and secondary isotope effects as well as the effect of only 96% labelling of the deuterated terphenyl could not be evaluated in this investigation.

4.3 - EFFECT OF RADIOLYSIS

4.3.1 - m-TERPHENYL DECREASE

The decrease of the starting m-terphenyl can, both for the radiolysis of labelled and of unlabelled material, be described as resulting from a higher than zero order reaction. The limited experimental data did not allow the assignment of a more precise reaction order.

With the same experimental conditions, the decomposition of m-terphenyl-d_{14} is 48 % less than that of unlabelled material.

4.3.2 - QUINQUA- AND HEXAPHENYL FORMATION

The formation of quinqua- and hexaphenyls from the radiolysis of both m-terphenyl and m-terphenyl-d_{14} can be described as resulting from a higher than zero order reaction. Our experimental data did not allow a reliable determination of the exact reaction order.

Compared with the quinqua- and hexaphenyl formation from the radiolysis of unlabelled m-terphenyl a 60% decreased rate is observed for the radiolysis of deuterated m-terphenyl.

There are only traces of quaterphenyls present in this high boiling fraction. The main reaction products are hexaphenyls and other compounds of the C_{36}-region.

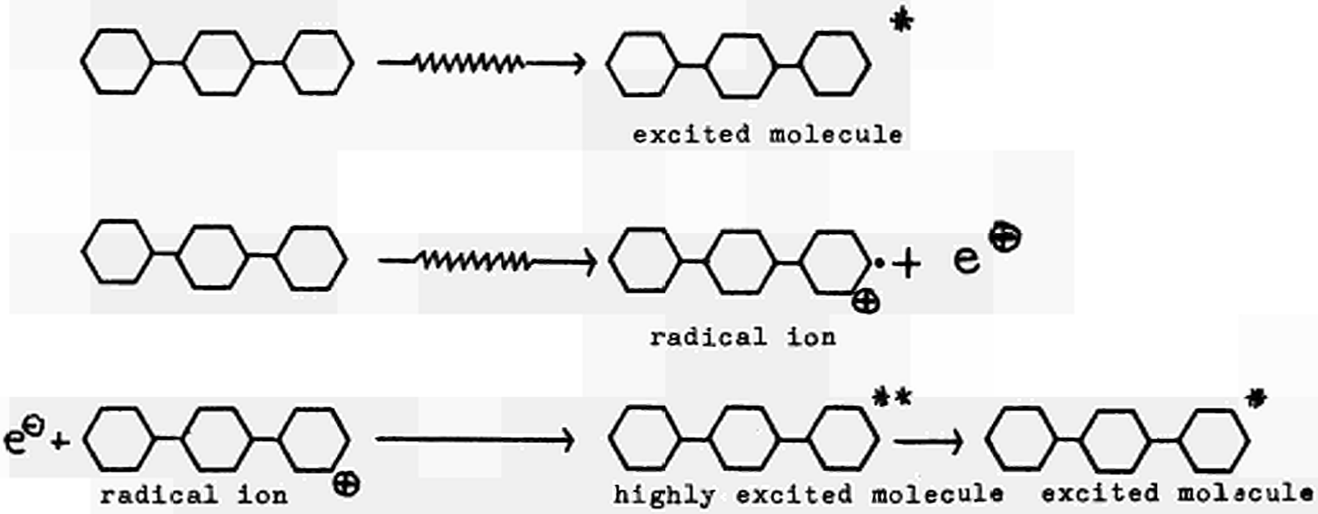
4.3.3 - HIGH HIGH BOILER FORMATION

The formation of high high boilers, consisting of p,p-hexaphenyl and compounds of higher molecular weight than hexaphenyls also results from a higher than zero order reaction. Compared with the product formation originating from the radiolysis of unlabelled m-terphenyl a 50% reduced rate is observed for the formation of high high boilers from deuterated m-terphenyl.

4.4 - REACTION MECHANISM OF THE RADIOLYSIS OF m-TERPHENYL AND m-TERPHENYL-d_{14}

In order to understand the quantitative differences between the radiolysis of unlabelled and deutero-terphenyl, we have to consider the primary energy absorptions of the ground state molecules and the consecutive secondary process of the return of the excited molecules and ions to ground state in more detail.

It is commonly agreed that ionizing radiation produces excited molecules in matter directly and also indirectly by neutralisation of intermediate ions. For the terphenyl radiolysis the following processes would be expected:



The normal state of an unexcited molecule is represented by the lowest vibrational level of the ground state, where the vibrational quantum number is zero and the molecule has only zero point vibrational energy.

Absorption of radiation can raise the molecule to the first or higher excited states supplying the molecule with potential energy. Potential energy in this context comprises the electronic energy associated with higher electron orbits, the vibrational energy of two molecular parts (e.g. D and rest terphenyl) as they move together and apart, and rotational energy.

Aromatic CD-bonds possess an app. 1,2 kcal/mole[x)] lower zero point energy of CD-vibrations than the aromatic CH-bonds for CH-vibrations in m-terphenyl. Quantitative differences resulting in a higher radiolytic stability of the deuterated compound should therefore exist between comparable energy absorption processes of hydrogen or deuterium containing terphenyl molecules; higher energy quanta are necessary to raise a deutero-molecule to the same excited state with the same potential energy as a terphenyl containing only hydrogen.

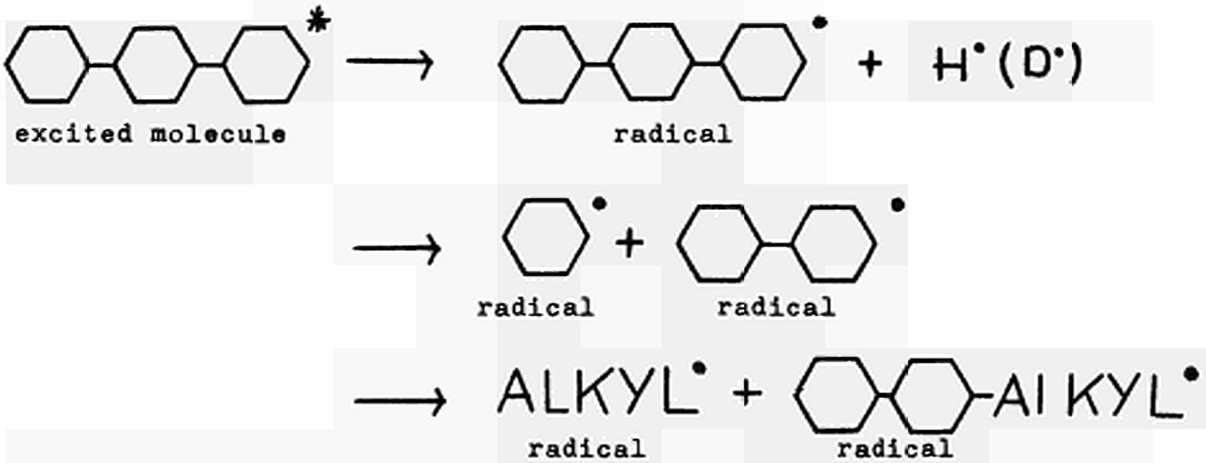
Being once formed, excited labelled and unlabelled m-terphenyl molecules should also show quantitative differences in returning to ground state conditions. This should show up for the physical means, being

a) fluorescence (radiative conversion to the ground state)
b) internal conversion (non radiative conversion to a lower state of the same multiplicity)
c) intersystem crossing (non radiative conversion to a state of different multiplicity)
d) non radiative energy transfer to a neighboring molecule.

[x)] We are grateful to Dr. S. Sandroni, who determined the zero point energy of m-terphenyl (17o ± 5 kcal/mole) and m-terphenyl-d_{14} (135 ± 5 kcal/mole).

It should also be valid for the chemical means. They are even more important in this context, because they explain the final product formation. The following reaction steps are postulated for the polyphenyl radiolysis:

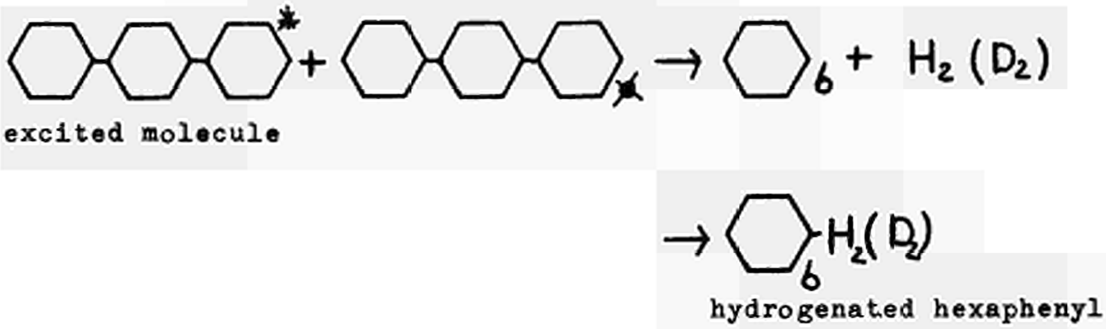
a) Unimolecular reactions:

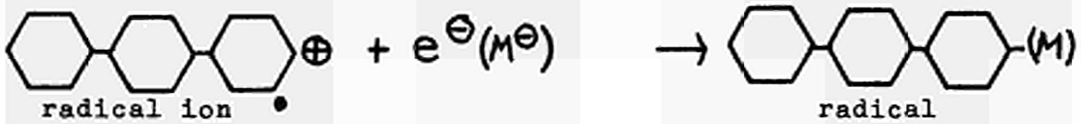


CH- and CD-bond ruptures respectively are the most likely of the dissociation processes. The CH- and the CD-bond dissociation energies will be smaller for the excited states of the molecules than for the ground states, The excited deuterated molecule will also have a higher bond strength than the excited unlabelled molecule. Consequently the chance of CD-breakages in the excited state of the deutero-terphenyl will be smaller than the chance of a CH-rupture of the unlabelled molecules.

A corresponding secondary isotope effect might account for differences in aromatic CC-bond ruptures or for CC-bond breakages between the aromatic rings.

b) Bimolecular reactions:





The first two addition reactions involve CH- and CD-bond breakages of the terphenyl molecules in the ground and/or the excited state. Due to the higher bond strength of the CD-bond compared to the CH-bond, the deuterated molecules should show a greater stability even in these reaction steps.

c) Secondary reactions:

The hydrogen atoms, deuterium atoms, and the phenyl-, diphenyl-, terphenyl- and alkyl-radicals formed during the unimolecular dissociation processes formulated above undergo further reactions with mother molecules. During these reaction steps new CH- resp. CD-bonds are broken. The differences in bond strength should also for these secondary reactions result in the preferred attack of the non-deuterated terphenyls.

5 - CONCLUSIONS

The following conclusions can be drawn from our investigations:

a) The over all decomposition for the pyrolysis of m-terphenyl at 425°C and 441°C is app. 2o% lower, when instead of the normal hydrogen containing material totally deuterated material is used. The activation energies for both processes are app. 6o kcal/mole.

b) The over all decomposition of m-terphenyl-d_{14} due to fast electron radiolysis is app. 48% smaller than that of unlabelled terphenyl under the same experimental conditions.

c) There are 2o and 22% less high boilers formed when pyrolyzing m-terphenyl-d_{14} instead of unlabelled material at 425°C and 441°C respectively. The high boiler fraction contains app. 38% quaterphenyls and other c_{24}-compounds.

d) There are app. 6o% less quinqua- and hexaphenyls and app. 5o% less high high boilers formed when irradiating m-terphenyl-d_{14} instead of unlabelled material with fast electrons.

e) There is 22% less benzene and 38% less diphenyl formed when pyrolyzing m-terphenyl-d_{14} instead of unlabelled material at 425°C and 441°C.

f) There are 3o% less quaterphenyl and other c_{24}-compounds formed when pyrolyzing m-terphenyl-d_{14} instead of unlabelled material. The composition of these fractions with respect to the individual components remains after the pyrolysis of labelled or unlabelled material app. the same.

g) There are only traces of benzene, terphenyl isomers, quaterphenyls and quinquaphenyls formed when irradiating deuterated or unlabelled m-terphenyl with fast electrons.

h) There are 55% less hydrogen and saturated and unsaturated aliphatic hydrocarbons formed when pyrolyzing m-terphenyl-d_{14} instead of unlabelled material.

i) The pyrolysis of deuterated m-terphenyl leads to app. the same over all decomposition and the same rates of product formations as the pyrolysis of unlabelled m-terphenyl at a temperature 5 - 7°C lower than applied for the thermal decomposition of unlabelled terphenyl.

6 - ACKNOWLEDGEMENT

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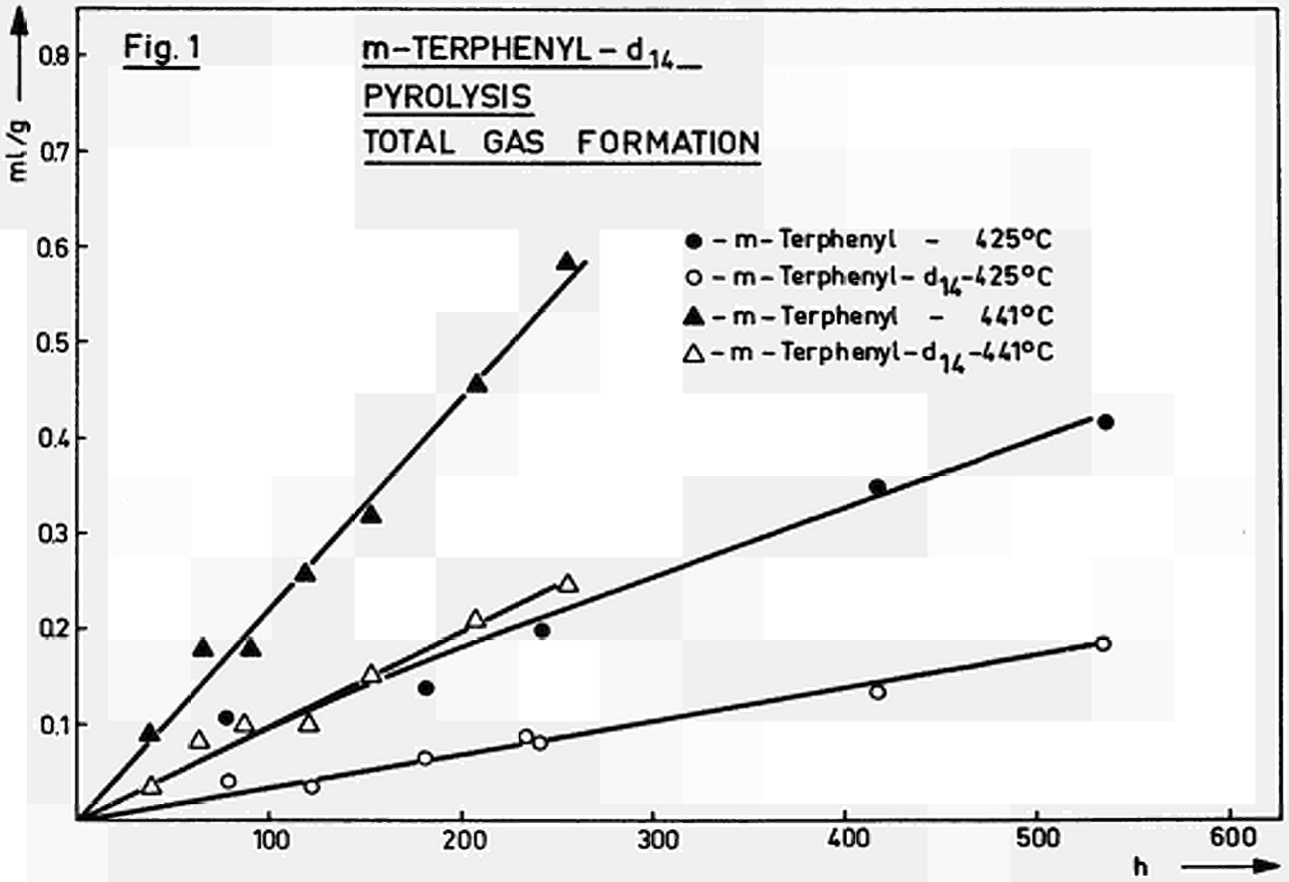


Fig. 1

m-TERPHENYL-d_{14}-
PYROLYSIS
TOTAL GAS FORMATION
● - m-Terphenyl - 425°C
○ - m-Terphenyl-d_{14}-425°C
▲ - m-Terphenyl - 441°C
△ - m-Terphenyl-d_{14}-441°C
ml/g
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
100
200
300
400
500
600
h

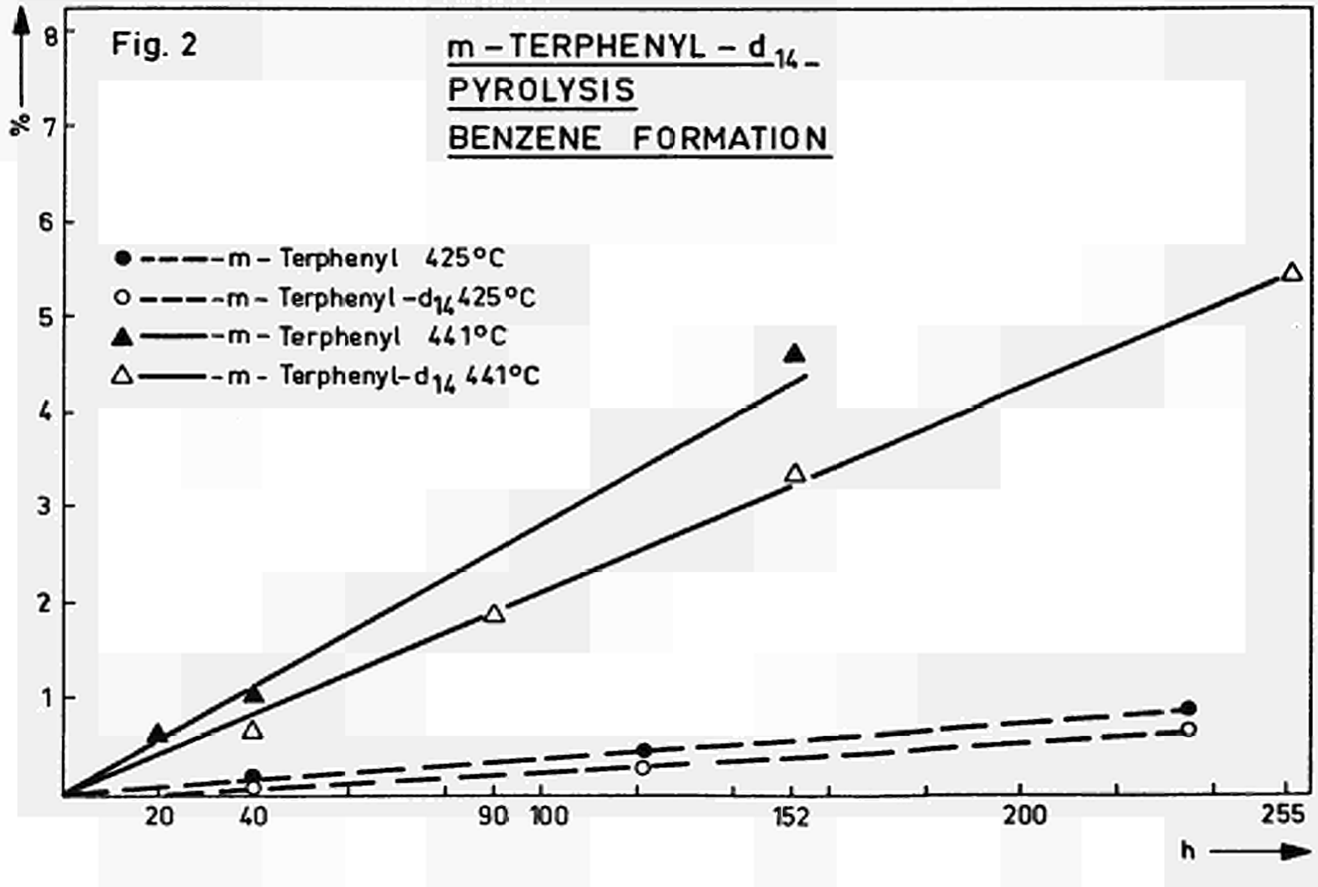


Fig. 2

m-TERPHENYL-d_{14}-
PYROLYSIS
BENZENE FORMATION
● ---- m-Terphenyl 425°C
○ ---- m-Terphenyl-d_{14} 425°C
▲ —— m-Terphenyl 441°C
△ —— m-Terphenyl-d_{14} 441°C
%
8
7
6
5
4
3
2
1
20
40
90
100
152
200
255
h

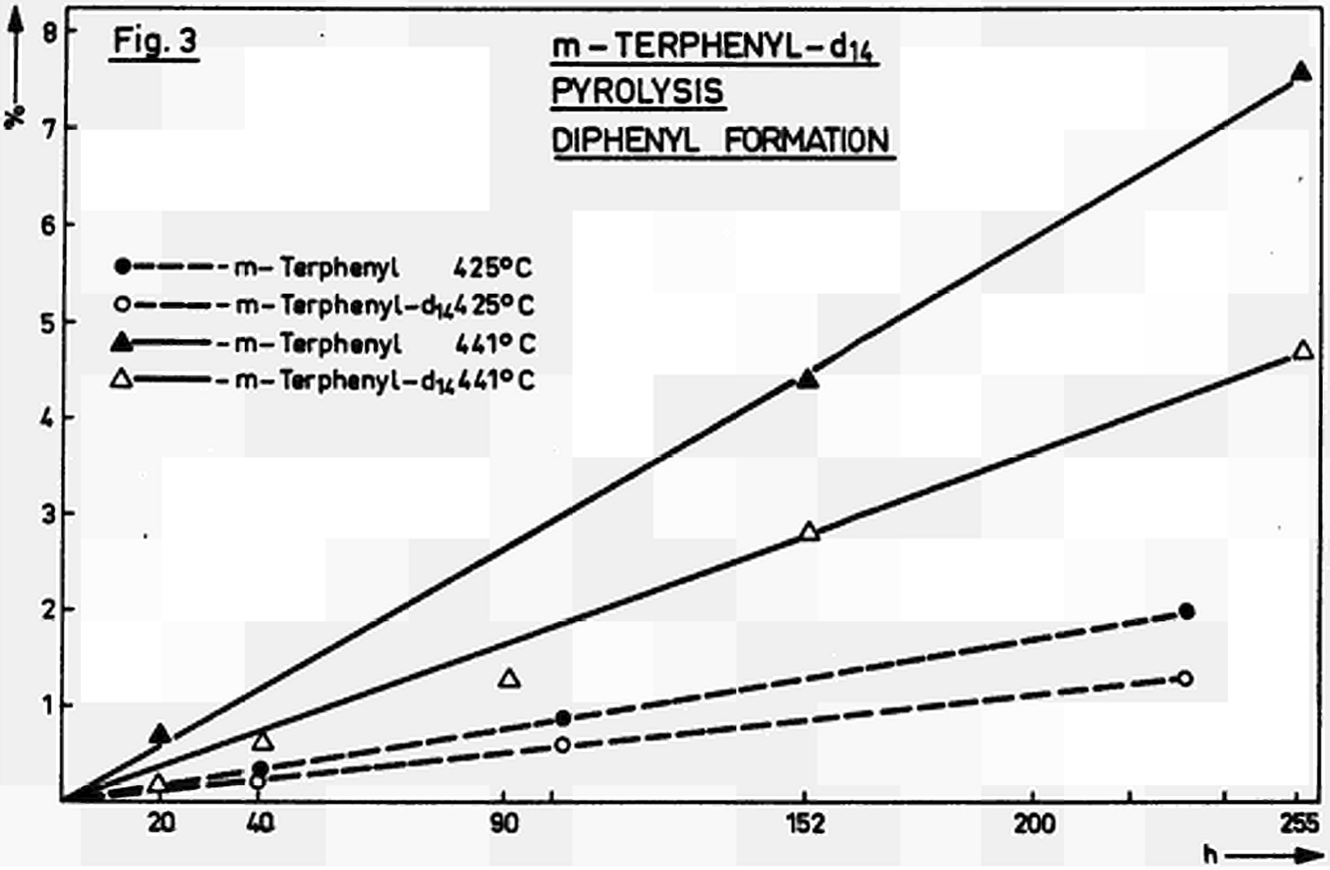


Fig. 3

m – TERPHENYL – d14
PYROLYSIS
DIPHENYL FORMATION
●– – – – m- Terphenyl 425°C
○– – – – m- Terphenyl-d14 425°C
▲——— m- Terphenyl 441°C
△——— m- Terphenyl-d14 441°C
%
8
7
6
5
4
3
2
1
20
40
90
152
200
255
h

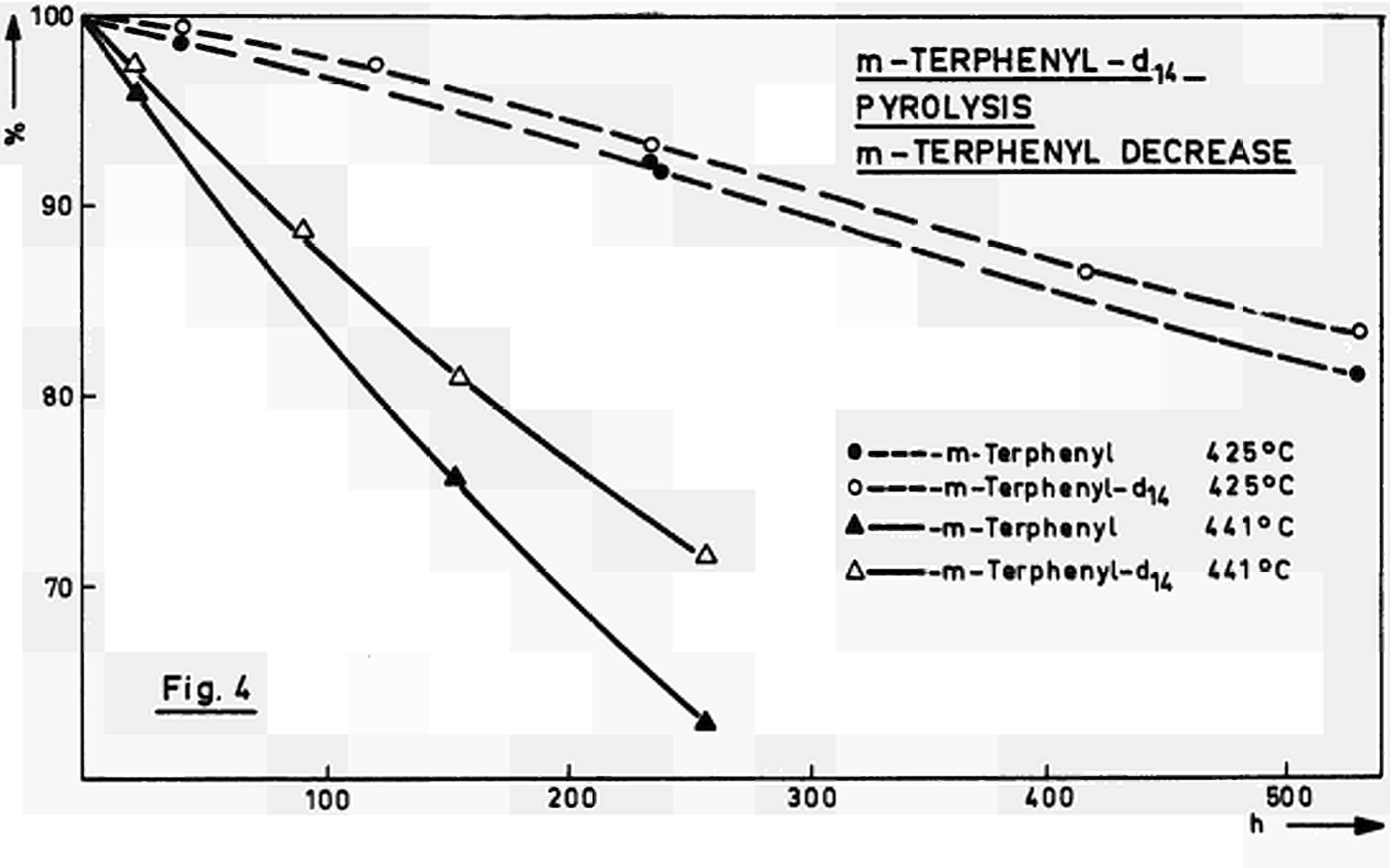


Fig. 4

m – TERPHENYL – d14
PYROLYSIS
m – TERPHENYL DECREASE
●– – – – m-Terphenyl 425°C
○– – – – m-Terphenyl-d14 425°C
▲——— m-Terphenyl 441°C
△——— m-Terphenyl-d14 441°C
%
100
90
80
70
100
200
300
400
500
h

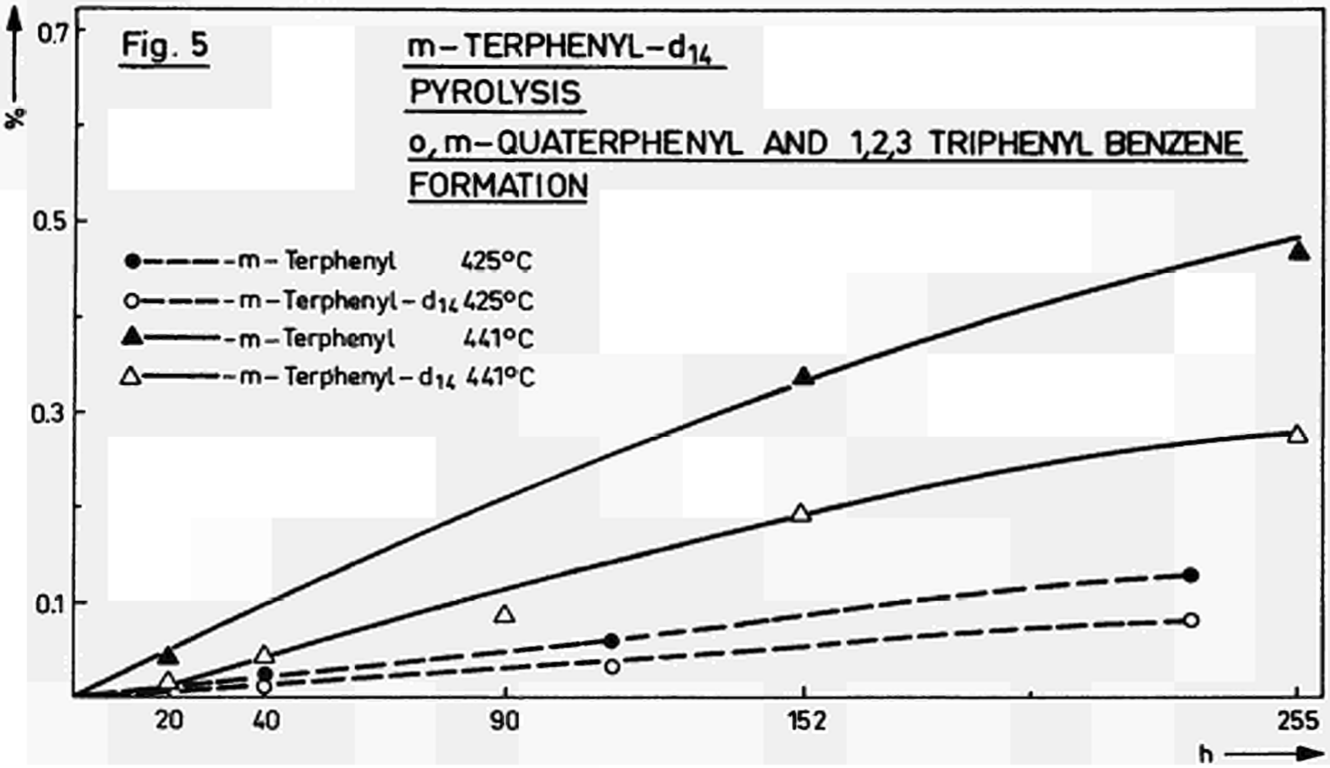


Fig. 5 m–TERPHENYL–d_{14} PYROLYSIS o, m–QUATERPHENYL AND 1,2,3 TRIPHENYL BENZENE FORMATION

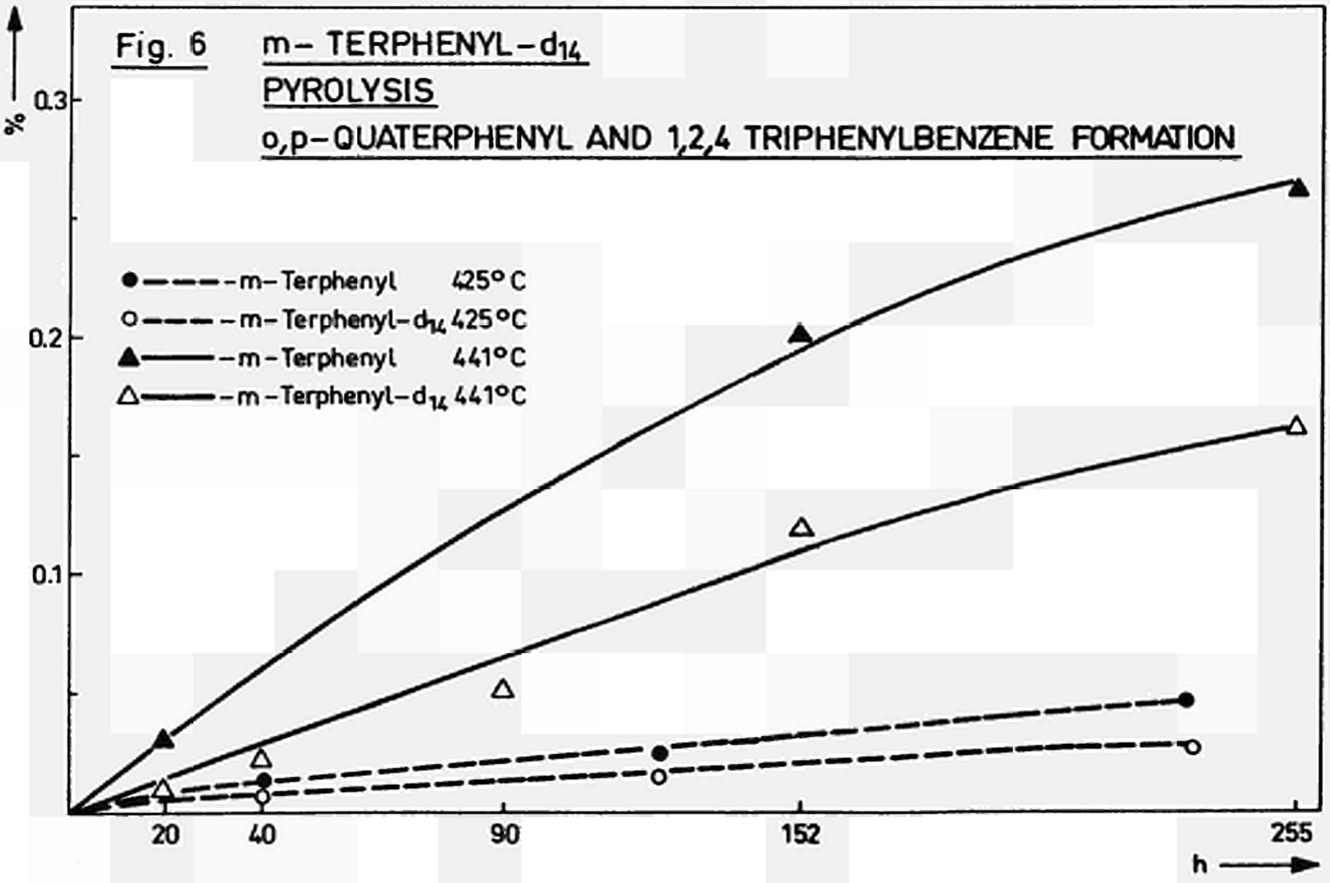


Fig. 6 m– TERPHENYL–d_{14} PYROLYSIS o,p–QUATERPHENYL AND 1,2,4 TRIPHENYLBENZENE FORMATION

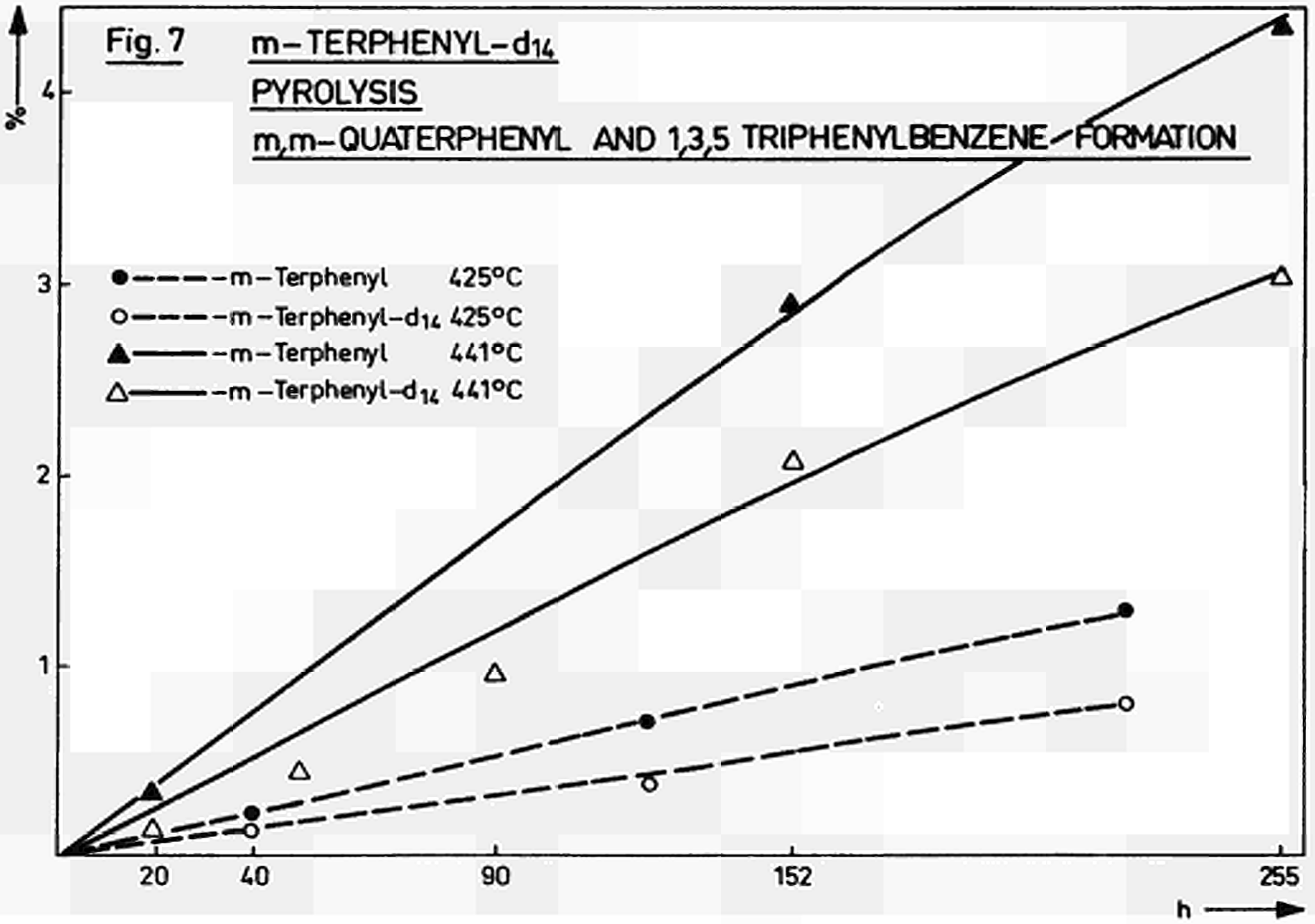


Fig. 7 m–TERPHENYL–d_{14}
PYROLYSIS
m,m–QUATERPHENYL AND 1,3,5 TRIPHENYLBENZENE FORMATION

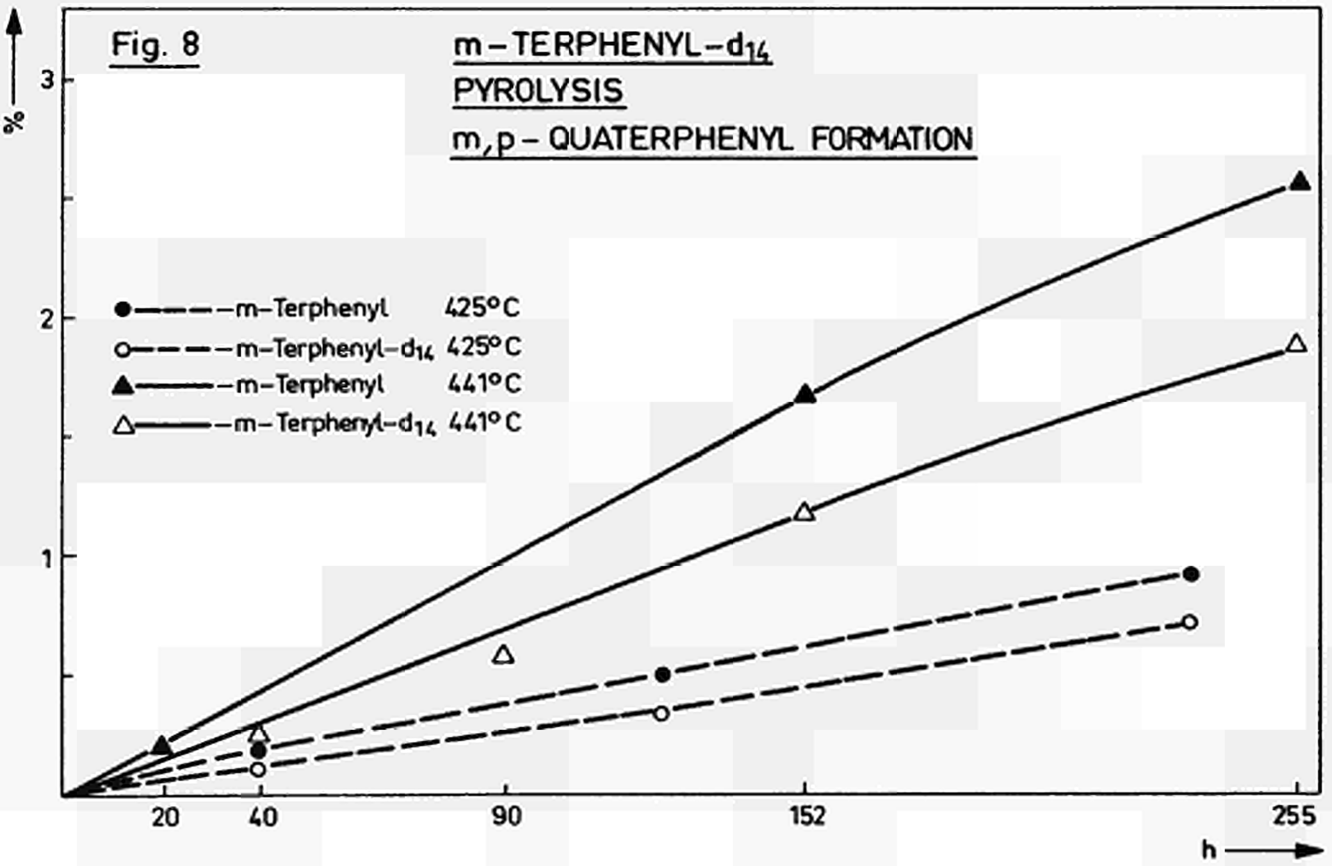


Fig. 8 m–TERPHENYL–d_{14}
PYROLYSIS
m,p–QUATERPHENYL FORMATION

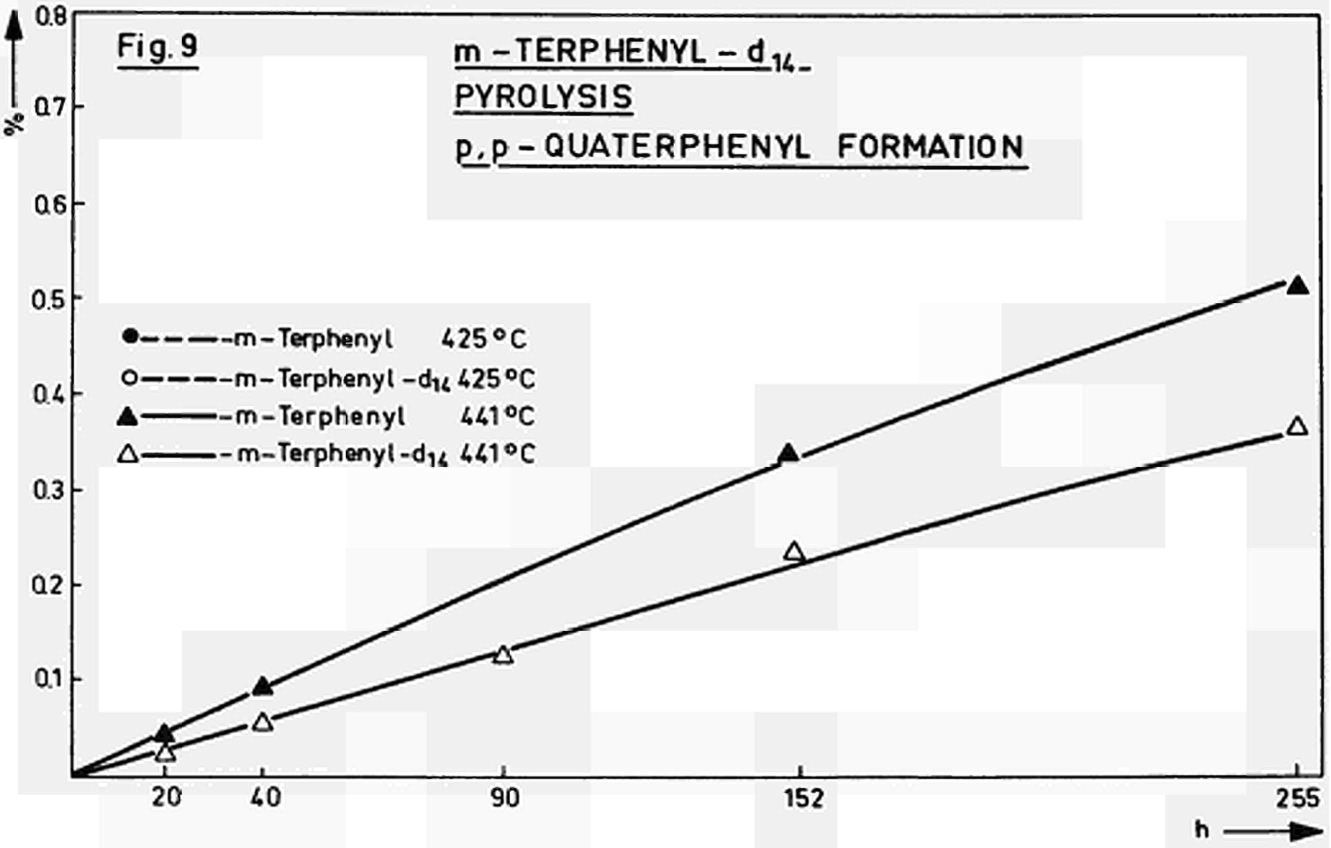


Fig. 9

m-TERPHENYL-d_{14}-PYROLYSIS

p,p-QUATERPHENYL FORMATION

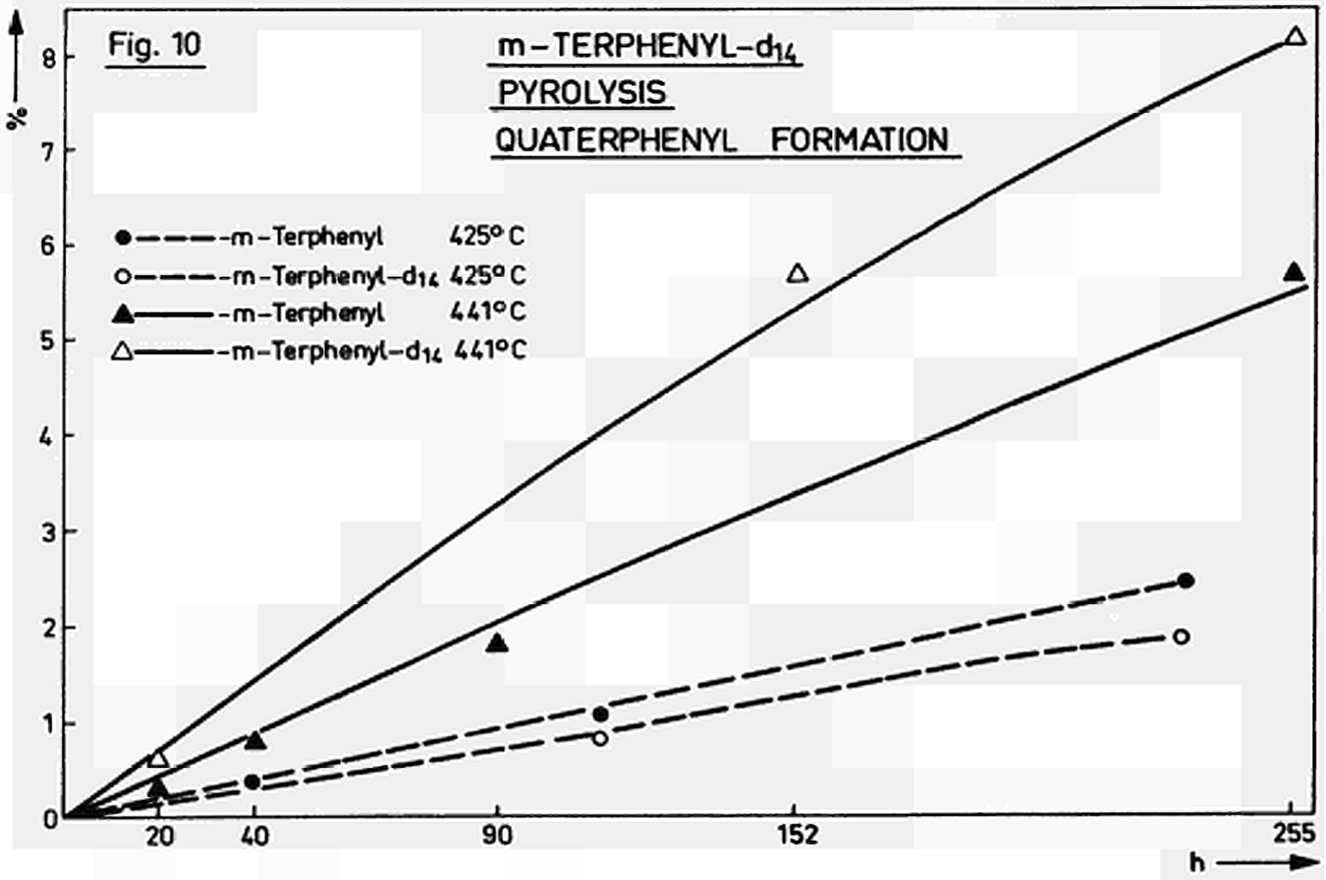


Fig. 10

m-TERPHENYL-d_{14}

PYROLYSIS

QUATERPHENYL FORMATION

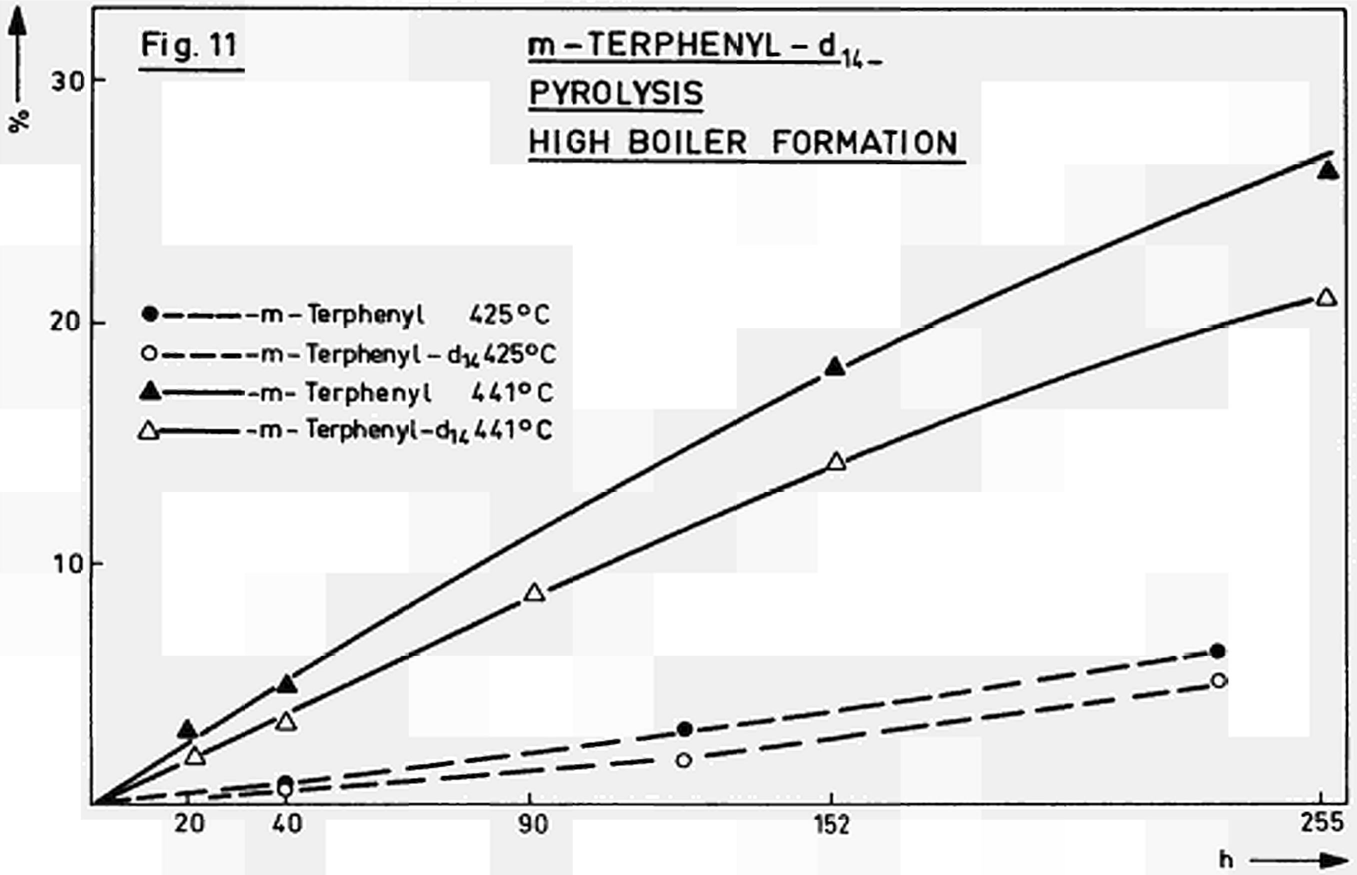


Fig. 11

m-TERPHENYL-d_{14}-
PYROLYSIS
HIGH BOILER FORMATION

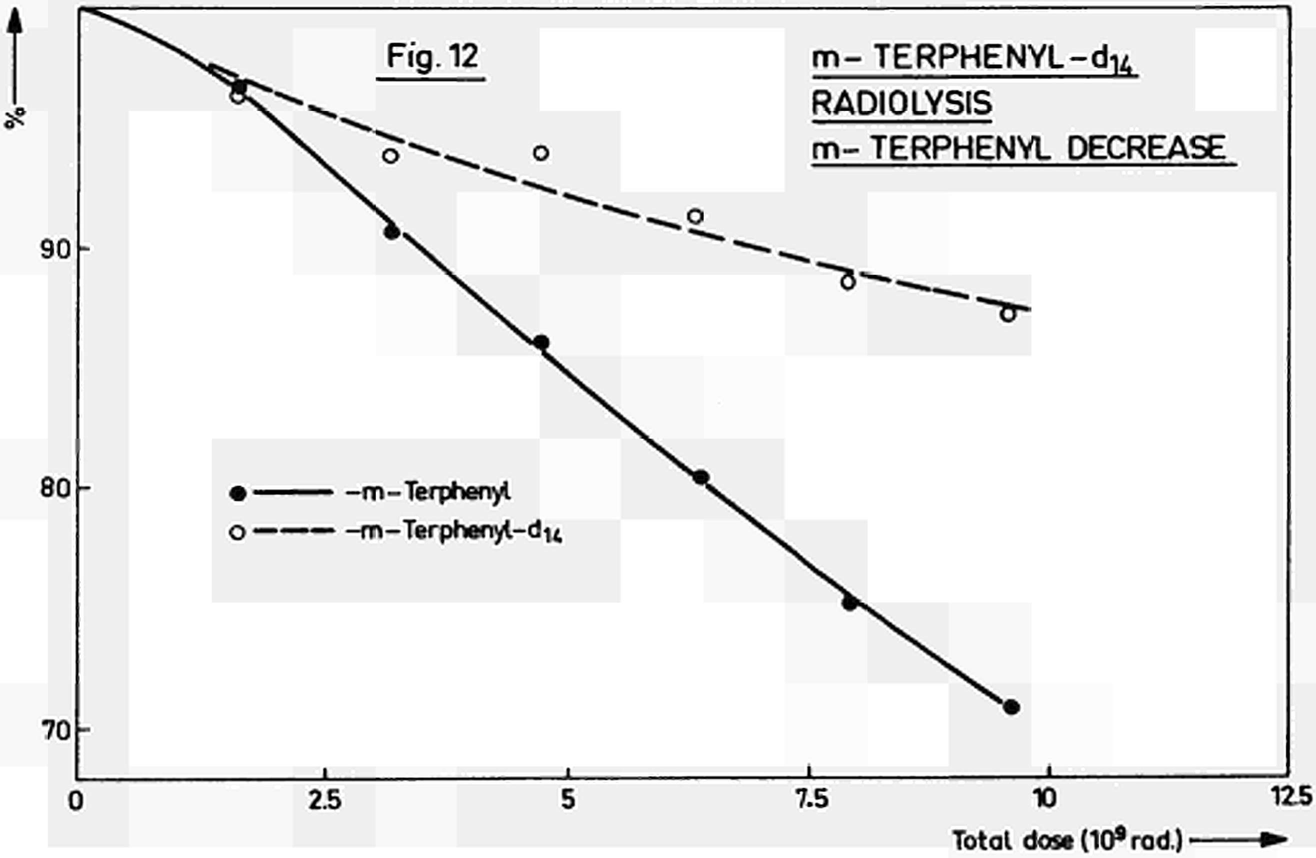


Fig. 12

m-TERPHENYL-d_{14}
RADIOLYSIS
m-TERPHENYL DECREASE

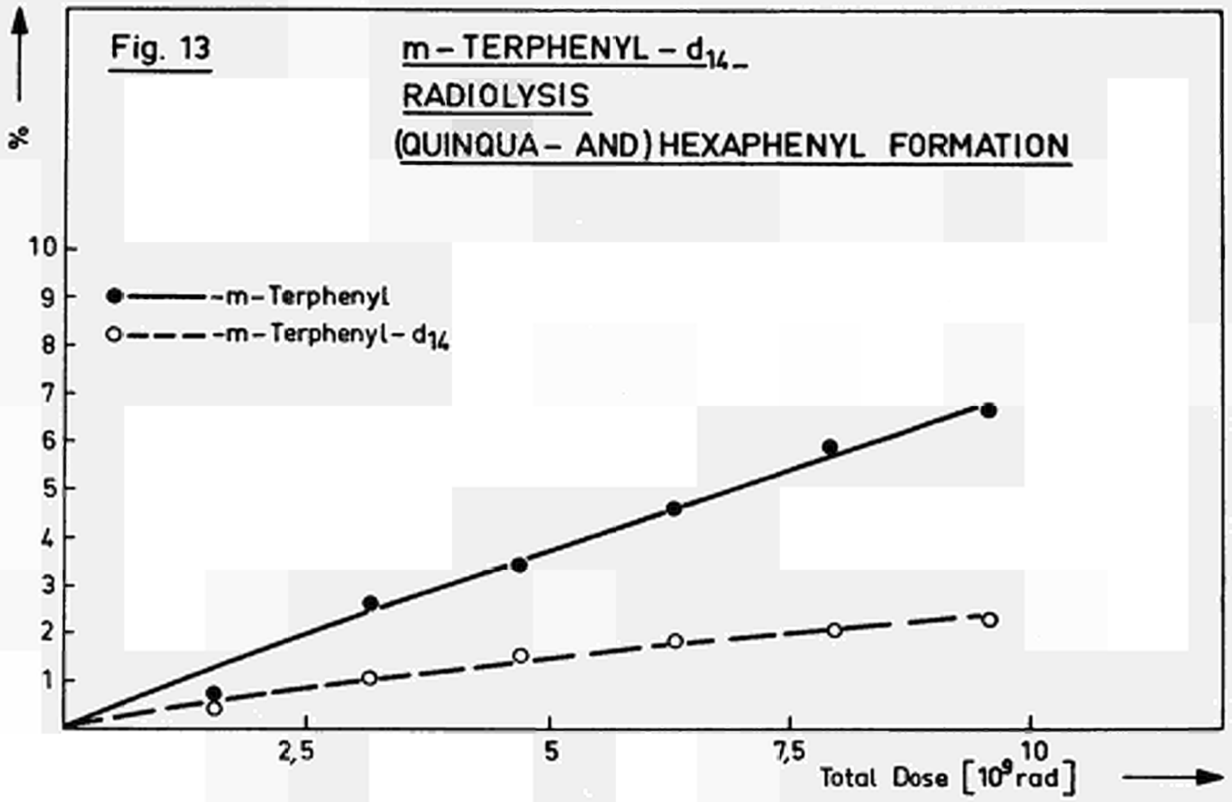


Fig. 13

m – TERPHENYL – d_{14} –
RADIOLYSIS
(QUINQUA – AND) HEXAPHENYL FORMATION

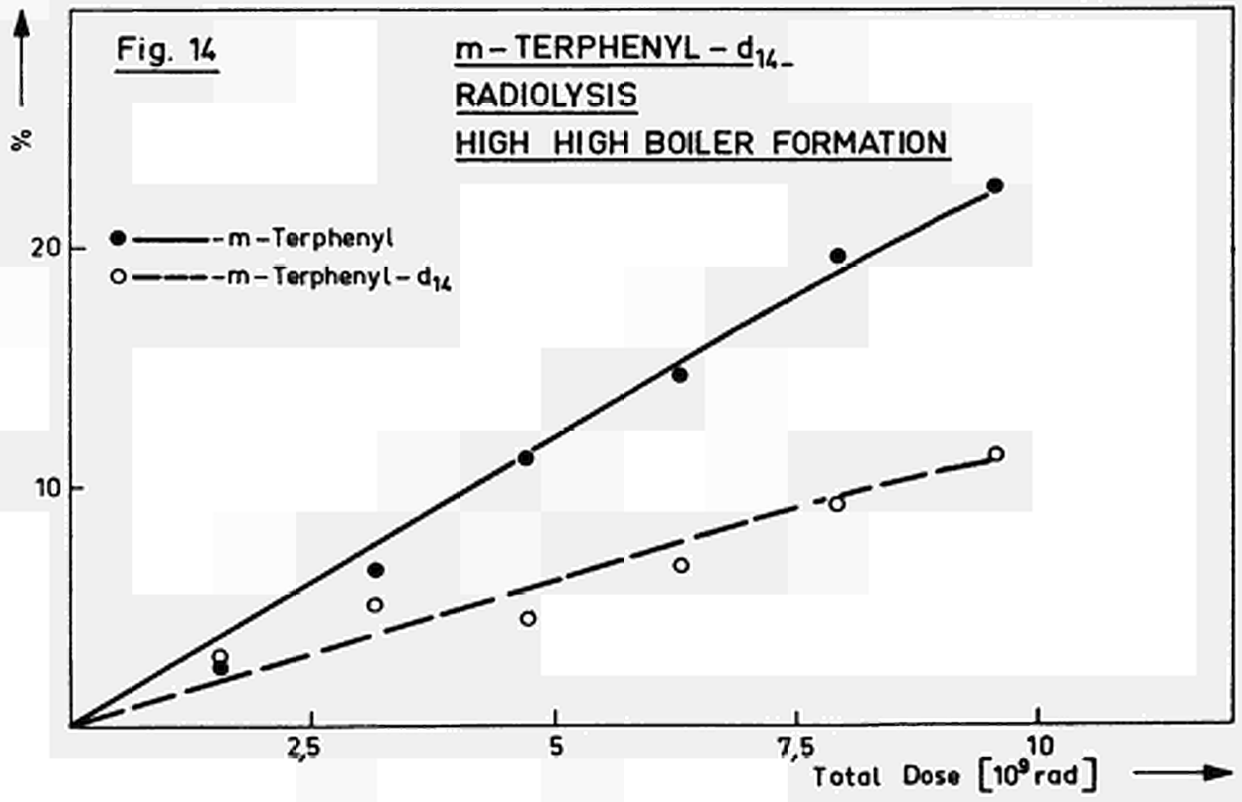
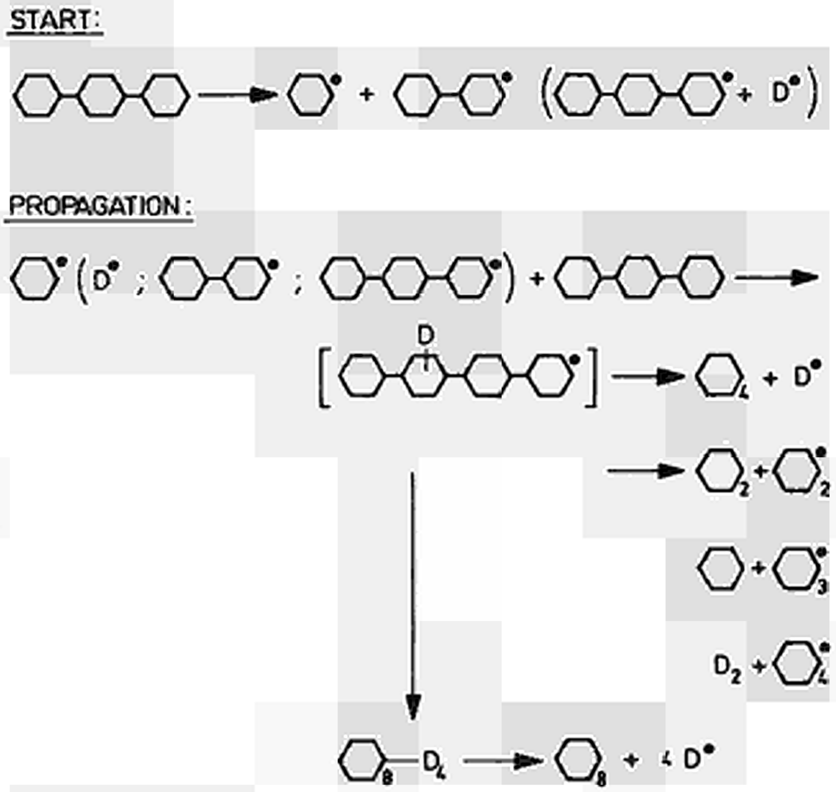


Fig. 14

m – TERPHENYL – d_{14} –
RADIOLYSIS
HIGH HIGH BOILER FORMATION

Fig 15

REACTION MECHANISM PYROLYSIS



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