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IDO-16876
May 1963

THE ELECTRON RADIOLYSIS OF BENZENE-M-TERPHENYL
AND PERDEUTEROBENZENE-M-TERPHENYL MIXTURES

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**NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION**

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Printed in USA

IDO-16876
AEC Research and Development Report
Reactor Technology
TID-4500 (19th Ed.)
Issued: May 1, 1963

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Contract AT(10-1)-1080
Idaho Operations Office

U. S. ATOMIC ENERGY COMMISSION

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SUMMARY

Mixtures of benzene (also perdeutero benzene) and m-terphenyl were irradiated with 6-Mev electrons. The primary polyphenyls products were biphenyl; o,m-, m,m-, and m,p-quaterphenyls; 1,2,3-, 1,2,4-, and 1,3,5-triphenylbenzenes; and approximately 21 of the possible hexaphenyls. The partial reactivities of the six distinguishable m-terphenyl positions were estimated from product distributions. Initial hexaphenyl product distributions were estimated for the radiolysis of m-terphenyl at 80°C.

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CONTENTS

SUMMARY	ii
I. INTRODUCTION	1
II. EXPERIMENTAL	1
III. RESULTS AND DISCUSSION	2
IV. REFERENCES	10

TABLES

I. Total Polyphenyl Yields from Perdeutero benzene Polyphenyl Mixtures	7
II. Quaterphenyl Yields from the Radiolysis of Benzene- M-Terphenyl and Perdeutero benzene-M-Terphenyl Mixtures	7
III. Reactive Species and Scavenging Probabilities of Irradiated M-Terphenyl; Partial Reaction Rates	8
IV. Predicted Initial Hexaphenyl Product Yields from the Irradiation of M-Terphenyl	10

THE ELECTRON RADIOLYSIS OF BENZENE-M-TERPHENYL AND PERDEUTEROBENZENE-M-TERPHENYL MIXTURES

I. INTRODUCTION

A model was proposed by Hutchinson et al for separating the relative reactivities of the three distinguishable positions of biphenyl. The relative positional reactivities were determined both for activated species formation and for scavenging reactions. A similar approach was used by the author which involved studying benzene-biphenyl mixtures [1].

The purpose of this research was to determine the relative reactivities of the six m-terphenyl positions with respect to activated species formation and scavenging reactions.

II. EXPERIMENTAL

The benzene (also perdeuterobenzene)-m-terphenyl mixtures were irradiated under the Linac at 80°C using 6-Mev (average) electrons. The irradiation time varied from two to three hours. Approximately one to two percent of the reactants were converted to product.

The m-terphenyl was purified as described previously [2]. Perdeuterobenzene of 99.5 percent isotopic purity was obtained from Volk Radio Chemical Co.

Benzene-m-terphenyl mixtures were placed in glass ampoules and degassed by a series of melt, freeze, and evacuation steps at 0.05 mm. The resultant samples were sealed and irradiated as described above.

The analyses were completed using gas-solid chromatography [3, 4]. Each irradiated sample of unknown composition was compared with known samples to obtain appropriate peak area correction factors. Two different types of columns were used. A five-foot, 20 percent LiCl (on firebrick) column was used to obtain total polyphenyl product yields and to separate 1,2,3-triphenylbenzene from p-terphenyl impurity. Five-foot columns packed with 35 to 50 percent CaCl_2 on firebrick were necessary to resolve the 1,3,5-triphenylbenzene and m,m-quaterphenyl peaks.

III. RESULTS AND DISCUSSION

The irradiation of pure m-terphenyl would be expected to produce as principal polyphenyl products 21 possible hexaphenyls. The first expected event should be the generation of a reactive species:

Each of the reactive species, a* for example, reacts with or is scavenged by m-terphenyl to produce hexaphenyls of the type noted in Equation (2):

Let $\underline{a}$, $\underline{b}$, $\underline{c}$, $\underline{d}$, $\underline{e}$, and $\underline{f}$ be the mole fraction yields of the a^* , b^* , etc, reactive species in Equation (1) such that:

$$a + b + c + d + e + f = 1.00 \quad (3)$$

A reactive species may be scavenged by any of the six distinguishable positions on m-terphenyl. Let $\underline{A}$, $\underline{B}$, $\underline{C}$, $\underline{D}$, $\underline{E}$, and $\underline{F}$ be the average probability that a given reactive species will be scavenged by each of the positions (respectively) noted in Equation (2). Thus,

$$A + B + C + D + E + F = 1.00 \quad (4)$$

A series of equations can be set up to describe the relative yields of each of the 21 hexaphenyl products in terms of reactive species and scavenging probabilities. For example, the mole fraction yield of m,o,m,m-hexaphenyl should be

$$Y_{m,o,m,m-\phi_6} = aB + bA \quad (5)$$

To evaluate these reactive species and scavenging probabilities, the relative yields of at least 11 of the hexaphenyl products must be determined. This is not analytically possible at this time.

However, the relative reactivities of the six m-terphenyl positions can be determined by studying the radiolysis of benzene-m-terphenyl and perdeutero-benzene-m-terphenyl mixtures. The basic mechanism appears to be

where $\underline{A}$, $\underline{B}$, $\underline{C}$, $\underline{D}$, $\underline{E}$, and $\underline{F}$ should be equivalent to those listed in Equations (2) and (4). Similarly,

Experimentally, using GSC analyses, the biphenyl yield, the individual quaterphenyl yields, and the total hexaphenyl yield can be measured and expressed on a mole fraction basis:

$$Y\phi_2 + \sum_1^6 Y\phi_4 + \sum_1^{21} Y\phi_6 = 1.00 \quad (8)$$

For the perdeuterobenzene and m-terphenyl mixtures, the initial polyphenyl product yields may be expressed as:

$$Y'\phi_2 + \sum_1^6 Y'\phi_4 + \sum_1^{21} Y'\phi_6 = 1.00 \quad (9)$$

Following a procedure described recently^[5], the reactive species and scavenging probabilities were related to initial polyphenyl product yields from irradiated benzene-m-terphenyl mixtures by:

$$Y\phi_2 = nN \quad (10)$$

$$\sum_1^6 Y\phi_4 = n(1-N) + (1-n)N \quad (11)$$

$$\sum_1^{21} Y\phi_6 = (1-n)(1-N) \quad (12)$$

Similarly, Equations (13), (14), and (15) were derived for the perdeuterobenzene-m-terphenyl system.

$$Y \phi_2 = nM \quad (13)$$

$$\sum_1^6 Y' \phi_4 = m(1-M) + (1-m)M \quad (14)$$

$$\sum_1^{21} Y' \phi_6 = (1-m)(1-M) \quad (15)$$

Where $\underline{n}$ and $\underline{m}$ refer to the probability of forming a ϕ_1^* species from benzene and perdeuterobenzene, respectively. $\underline{N}$ and $\underline{M}$ refer to the scavenging probabilities of benzene and perdeuterobenzene, respectively.

Using the relationships noted in Equations (3), (4), (6), (7), (10), (11), and (12), the yield of o,m-quaterphenyl from the benzene-m-terphenyl system should be:

$$Y_{o,m-\phi_4} = n(1-N)A + (1-n)aN \quad (16)$$

The two terms in Equation (16) arise from the two ways in which o,m- ϕ_4 can be formed. The first term gives the mole fraction yield of o,m-quaterphenyl which should result from benzene activated species attacking or being scavenged by the ortho position of m-terphenyl:

$$\underbrace{\left(\begin{array}{c} \text{probability} \\ \text{of forming} \\ \text{a } \phi_1^* \text{ reactive} \\ \text{species} \end{array} \right)}_n \quad \underbrace{\left(\begin{array}{c} \text{probability that} \\ \text{the reactive} \\ \text{species chooses} \\ \text{to react with m-}\phi_3 \end{array} \right)}_{(1-N)} \quad \underbrace{\left(\begin{array}{c} \text{probability that} \\ \text{the reactive} \\ \text{species reacts at} \\ \text{the ortho position} \\ \text{of m-}\phi_3 \end{array} \right)}_A$$

The second term in Equation (16) gives the mole fraction yield of o,m- ϕ_4 which should result from m-terphenyl molecules activated in the ortho position (a*) attacking or being scavenged by benzene:

$$\underbrace{\left(\begin{array}{c} \text{probability} \\ \text{of forming} \\ \text{a m-}\phi_3^* \\ \text{reactive species} \end{array} \right)}_{(1-n)} \quad \underbrace{\left(\begin{array}{c} \text{probability that} \\ \text{the m-}\phi_3^* \text{ reactive} \\ \text{species is activated} \\ \text{in the ortho position} \end{array} \right)}_a \quad \underbrace{\left(\begin{array}{c} \text{probability that} \\ \text{the reactive} \\ \text{species will react} \\ \text{with benzene} \end{array} \right)}_N$$

Similarly, the o,m-quaterphenyl yield from the perdeuterobenzene-m-terphenyl system should be:

$$Y'_{o,m-\phi_4} = m(1-M)A + (1-m)AM \quad (17)$$

By substituting the values of $\underline{n}$, $\underline{N}$, $\underline{m}$, and $\underline{M}$ [calculated from Equations (10) to (15)] into Equations (16) and (17), $\underline{a}$ and $\underline{A}$ can be evaluated. Similarly, the following sets of simultaneous equations may be solved to yield: b, B, c, C, d, D, e, E, f, and F.

$$Y_{m,m-\phi_4} = n(1-N)B + (1-n)Nb \quad (18)$$

$$Y'_{m,m-\phi_4} = m(1-M)B + (1-m)Mb \quad (19)$$

$$Y_{m,p-\phi_4} = n(1-N)C + (1-n)Nc \quad (20)$$

$$Y'_{m,p-\phi_4} = m(1-M)C + (1-m)Mc \quad (21)$$

$$Y_{1,2,3-\phi_3}Bz = n(1-N)D + (1-n)Nd \quad (22)$$

$$Y'_{1,2,3-\phi_3}Bz = m(1-M)D + (1-m)Md \quad (23)$$

$$Y_{1,2,4-\phi_3}Bz = n(1-N)E + (1-n)Ne \quad (24)$$

$$Y'_{1,2,4-\phi_3}Bz = m(1-M)E + (1-m)Me \quad (25)$$

$$Y_{1,3,5-\phi_3}Bz = n(1-N)F + (1-n)Nf \quad (26)$$

$$Y'_{1,3,5-\phi_3}Bz = m(1-M)F + (1-m)Mf \quad (27)$$

Since each of the systems studied had somewhat different benzene/m-terphenyl and perdeuterobenzene/m-terphenyl mole ratios, the following relationships [5] were used to convert $n_{1.0}$, $N_{1.0}$ and also $m_{1.0}$ and $M_{1.0}$ to the appropriate activated species and scavenging probabilities.

$$\left(\frac{n}{1-n}\right) = \left(\frac{n_{1.0}}{1-n_{1.0}}\right) \left(\frac{\phi_1}{m-\phi_3}\right) \quad (28)$$

$$\left(\frac{N}{1-N}\right) = \left(\frac{N_{1.0}}{1-N_{1.0}}\right) \left(\frac{\phi_1}{m-\phi_3}\right) \quad (29)$$

$N_{1.0}$, $n_{1.0}$, $M_{1.0}$, and $m_{1.0}$ refer to equal molar benzene and m-terphenyl mixtures.

Table I lists duplicate analyses which were made to determine average $m_{1.0}$ and $M_{1.0}$ values. Average values for $n_{1.0}$ and $N_{1.0}$ were obtained from a previous report by the author [5].

Using the mole fraction quaterphenyl yields in Table II and the average $n_{1.0}$, $N_{1.0}$, $m_{1.0}$, and $M_{1.0}$ values listed in Table I, the reactive species and scavenging probabilities for each of the six distinguishable m-terphenyl positions

TABLE I

TOTAL POLYPHENYL YIELDS FROM PERDEUTEROBENZENE POLYPHENYL MIXTURES

(C ₆ D ₆ /m- ϕ ₃)	1.266	1.403
ϕ_2	0.060	0.063
$\sum_1^6 \phi_4$	0.382	0.399
$\sum_1^{21} \phi_6$	0.558	0.538
m	0.305	0.339
M	0.197	0.186
m _{1.0}	0.257	0.268
M _{1.0}	0.162	0.140

The values of m_{1.0} and M_{1.0} which were used in all the calculations are 0.263 and 0.151, respectively. The average n_{1.0} and N_{1.0} values which were used are 0.446 and 0.136, respectively.

TABLE II

QUATERPHENYL YIELDS FROM THE RADIOLYSIS OF BENZENE-M-TERPHEENYL AND PERDEUTEROBENZENE-M-TERPHEENYL MIXTURES

	<u>14B</u> <u>1</u>	<u>15A</u> <u>2</u>	<u>15D</u> <u>3</u>	<u>86B</u> <u>4</u>	<u>15B</u> <u>5</u>	<u>15C</u> <u>6</u>
(C ₆ H ₅ /m- ϕ ₃)	-	-	-	1.342	1.396	1.303
(C ₆ D ₆ /m- ϕ ₃)	1.252	1.266	1.403	-	-	-
1,2,3- ϕ_3 Bz	0.0254	0.0240	0.0279	0.0242	0.0309	0.0403
o,m- ϕ_4	0.0865	0.0818	0.0855	0.1063	0.1111	0.1081
1,2,4- ϕ_3 Bz	0.0768	0.0804	0.0823	0.1131	0.1164	0.1091
m,m- ϕ_4	0.0856	0.0883	0.0958	0.1011	0.1093	0.1017
1,3,5- ϕ_3 Bz	0.0179	0.0176	0.0192	0.0217	0.0236	0.0208
m,p- ϕ_4	0.0907	0.0824	0.0956	0.1256	0.1136	0.1148
$\sum_1^6 Y\phi_4$	0.3829	0.3745	0.4063	0.4920	0.5049	0.4948

were determined. These results, listed in Table III, were determined by comparing each of the perdeuterobenzene samples with each of the three benzene samples.

TABLE III

REACTIVE SPECIES AND SCAVENGING PROBABILITIES
OF IRRADIATED M-TERPHENYL; PARTIAL REACTION RATES

a	0.219 ± 0.029*	A	0.218 ± 0.008
b	0.309 ± 0.034	B	0.186 ± 0.015
c	0.207 ± 0.060	C	0.244 ± 0.029
d	0.074 ± 0.049	D	0.061 ± 0.029
e	0.136 ± 0.031	E	0.249 ± 0.012
f	0.056 ± 0.007	F	0.041 ± 0.014
r _a	0.71	k _A	1.17
r _b	1.00	k _B	1.00
r _c	1.34	k _C	2.62
r _d	0.96	k _D	1.31
r _e	0.88	k _E	2.68
r _f	0.72	k _F	0.88

*Standard deviation.

Partial reaction rates were computed using the following:

$$\begin{aligned}
 r_a &= \frac{a}{b} & r_d &= \frac{4d}{b} \\
 r_b &= \frac{b}{b} & r_e &= \frac{2e}{b} \\
 r_c &= \frac{2c}{b} & r_f &= \frac{4f}{b}
 \end{aligned} \tag{30}$$

$$\begin{aligned}
 k_A &= \frac{A}{B} & k_D &= \frac{4D}{B} \\
 k_B &= \frac{B}{B} & k_E &= \frac{2E}{B} \\
 k_C &= \frac{2C}{B} & k_F &= \frac{4F}{B}
 \end{aligned} \tag{31}$$

Thus, each of the individual positions may be compared to the meta position with regard to reactive species formation and scavenging reaction. These partial reaction rates are listed in Table III.

The values calculated for A, B, C, etc, represent the probability that an activated benzene species will be scavenged by each of the positions; or these values measure the relative reactivity of each of the m-terphenyl positions with respect to attack by an activated benzene species. If one assumes that other activated species such as a*, b*, etc, attack the m-terphenyl molecule with the same relative frequency as the benzene reactive species, then the data in Table III can be used to predict the initial hexaphenyl product distribution obtained from the irradiation of pure m-terphenyl.

Using Equation (5) and similar equations such as:

$$Y_{m,m,m,m-\phi_6} = bC + cB \quad (32)$$

$$Y_{m,m,m-\phi_6} = bB \quad (33)$$

$$Y_{m,o,p,m-\phi_6} = aC + cA \quad (34)$$

$$Y_{m,o,o,m-\phi_6} = aA \quad (35)$$

$$Y_{m,p,p,m-\phi_6} = cC \quad \text{etc} \quad (36)$$

The relative hexaphenyl yields from pure m-terphenyl were calculated and are listed in Table IV.

The second column in Table IV represents Hutchinson's predicted hexaphenyl distribution (for m-terphenyl radiolysis at 80°C). These predictions were based upon biphenyl partial rate factors (1) and the principle of additivity [6].

For example, it was assumed that:

$$\begin{aligned} k_D &= k_A^2 & r_d &= r_a^2 \\ k_E &= k_A k_C & r_e &= r_a r_c \\ k_F &= k_B^2 & r_f &= r_b^2 \end{aligned} \quad (37)$$

where k_A , k_B , and k_C refer to the scavenging partial rate factors of the ortho, meta, and para position of biphenyl, respectively; and k_D , k_E , and k_F are the predicted partial rate factors for the three distinguishable positions on the center ring of m-terphenyl. The k_A , k_B , and k_C biphenyl values are assumed to be the same for m-terphenyl. The agreement between the two predicted hexaphenyl distributions in Table IV indicates that the additivity principle may be reasonably accurate for product predictions in complicated polyphenyl radiolytic studies.

TABLE IV

PREDICTED INITIAL HEXAPHENYL PRODUCT YIELDS
FROM THE IRRADIATION OF M-TERPHENYL

	From m- ϕ_3 data	From ϕ_2 data
1. m,p,m,m-hexaphenyl	11.4	9.1
2. m,o,m,m-hexaphenyl	10.7	10.9
3. 2,4-diphenyl-3'-(3-xenyl)-biphenyl	10.2	11.7
4. m,o,p,m-hexaphenyl	9.9	9.0
5. 2,4-diphenyl-4'-(3-xenyl)-biphenyl	8.5	7.1
6. 2,4-diphenyl-2'-(3-xenyl)-biphenyl	8.4	11.0
7. m,m,m,m-hexaphenyl	5.8	4.8
8. m,p,p,m-hexaphenyl	5.1	3.1
9. m,o,o,m-hexaphenyl	4.6	5.8
10. 2,2',4,4'-tetraphenyl-biphenyl	3.4	3.8
11. 2,6-diphenyl-3'-(3-xenyl)-biphenyl	3.3	3.3
12. 2,6-diphenyl-4'-(3-xenyl)-biphenyl	3.1	2.4
13. 2,6-diphenyl-2'-(3-xenyl)-biphenyl	3.0	3.3
14. 2,6,2',4'-tetraphenyl-biphenyl	2.7	2.7
15. 3,5-diphenyl-3'-(3-xenyl)-biphenyl	2.3	2.4
16. 3,5-diphenyl-4'-(3-xenyl)-biphenyl	2.2	2.3
17. 3,5-diphenyl-2'-(3-xenyl)-biphenyl	2.1	2.7
18. 2,4,3',5'-tetraphenyl-biphenyl	2.0	2.9
19. 2,6,3',5'-tetraphenyl-biphenyl	0.6	0.8
20. 2,6,2',6'-tetraphenyl-biphenyl	0.5	0.4
21. 3,5,3',5'-tetraphenyl-biphenyl	0.2	0.3

Improved analytical procedure and known hexaphenyls for reference compounds would allow a direct and complete solution of the m-terphenyl problem. This work covers just one aspect of the extremely complicated radiation chemistry of polyphenyls. However, the approach can be expanded to include the formation and fate of hydroaromatics, the production of hydrogen and gaseous hydrocarbons, and secondary product formation when the data become available.

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