The Decomposition of Aromatic Substances by Different Kinds of Radiation

Part 2. The Radiolysis of Benzene, Biphenyl, and Orthoterphenyl with Particles from the ^{10}B(n,α) Reaction

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Received 28*th May*, 1962

Benzene, biphenyl, and orthoterphenyl, were irradiated with particles from the ^{10}B(n, α) reaction by exposing dilute solutions of boron compounds to thermal neutrons in the BEPO pile. The product yield per unit mass of the substance irradiated for a given thermal neutron dose was a linear function of the boron concentration, indicating additivity of the effects of the background pile radiation and the induced nuclear reaction. G values for the ^{10}B(n, α) particles calculated from the slopes of the linear graphs were essentially the same for two different boron compounds. Values at 25°C for benzene were $G(H_2) = 0{\cdot}57$, $G(C_2H_2) = 0{\cdot}26$, $G(-C_6H_6) = 2{\cdot}1$, and there was little variation with temperature up to 80°C. G values for biphenyl at 100°C were $G(H_2) = 0{\cdot}17$, $G(-C_{12}H_{10}) = 1{\cdot}52$, and for orthoterphenyl at 80-100°C, $G(H_2) = 0{\cdot}19$, $G(-C_{18}H_{14}) = 0{\cdot}93$. All these values are greater than those for fast electrons by factors ~10 or more, except for $G(-C_6H_6)$, which is greater by a factor ~2. G values for the pile radiation, obtained using previous calorimetric data, were intermediate between those for fast electrons and those for the ^{10}B(n, α) particles. The large variations in $G(-M)$ for biphenyl and orthoterphenyl are attributed to the competing reactions of excited molecules rather than radicals.

The first paper of this series [1] dealt with the irradiation of benzene with protons. In order to subject benzene to radiation of very high LET, dilute solutions were made of triphenyl boron, and tri-α-naphthyl boron, in benzene, and these were irradiated with slow neutrons in the BEPO pile to obtain the ^{7}Li+α particles of the B(n, α) reaction. Experiments with fast electrons and γ radiation had shown that with these radiations the boron compounds at the concentrations used had a negligible effect on the decomposition. Similar experiments were done with biphenyl and orthoterphenyl. The method is analogous to the exposure of aqueous solutions containing boric acid to slow neutrons.[2, 3] The energy deposited may be calculated from the measured thermal neutron flux, the concentration of boron, and the known constants of the nuclear reaction. Preliminary results have already been reported for benzene.[4, 5]

EXPERIMENTAL

MATERIALS

Benzene was purified as described previously [1]. Biphenyl and orthoterphenyl from L. Light and Co. were purified by passing a solution in 40-60°C petroleum ether through a silica/alumina column, with continuous refluxing of the solvent,[6] followed by recrystallization from the solvent, which was removed by distillation *in vacuo*.

Triphenyl boron from L. Light and Co. was distilled *in vacuo* in a sealed apparatus. The first fraction was rejected. The main fraction was collected in a tube which could be pulled off without breaking the vacuum. Above 170°C a yellow material began to distil and distillation was stopped. The main fraction consisted of white needle crystals. This substance is attacked by air and moisture, and was weighed out in a dry nitrogen-filled glove-box into silica capillary tubes, open at both ends. These were stored in the glove box, until used, in nitrogen filled tubes tightly sealed with rubber bungs.

Tri-α-naphthyl boron was prepared by the reaction of the Grignard reagent of α-bromonaphthalene with boron trifluoride etherate. The final m.p. was 205-206½° (cf. 206-207° [7]). No special precautions were taken during weighing as this substance is stable in air.

Boron Analysis.—The method of Hunter, Petterson and Steinberg [8] gave reproducible results which agreed with the theoretical composition.

Ampoule preparation. (see fig. 1).—Benzene, previously outgassed and dried over calcium hydride, was contained in the flask D_1. Silica capillaries containing weighed amounts of triphenyl boron were introduced at openings E, which were quickly sealed and the apparatus evacuated. Constrictions C_3 were wide enough to allow passage of the capillaries. The break-seal was broken and the benzene was outgassed in flask D_1 and distilled into flask D_2 where it was thoroughly outgassed after sealing C_1. Constriction C_2 was sealed and the benzene distilled successively into the silica vessels G joined to the Pyrex glass apparatus by graded seals at F. Each sample was pulled off at C_3 and the benzene gently refluxed to wash the triphenyl boron into the ampoule. The solution was finally frozen and the ampoule sealed off at C_4. The benzene present was determined later by weighing. Sample masses were 2 to 6 g.

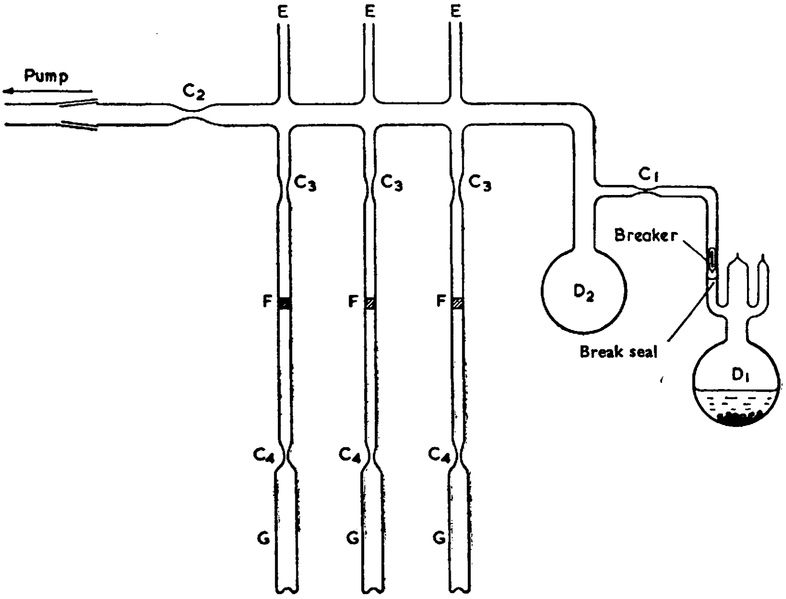

FIG. 1.—Diagram of cell filling apparatus.

For tri-α-naphthyl boron the tubes E were omitted and the tube between C_3 and F was not joined until the substance was introduced into the tube by pouring it from a weighing tube. The maximum concentration of either boron compound was equivalent to 784 p.p.m. of boron.

Similar methods were used for making solutions in biphenyl and in orthoterphenyl, but in these cases the solid solvent was weighed into a flask before degassing, and each sample was prepared individually. Sample masses were all 4 g; with maximum boron concentrations of 420 p.p.m. for biphenyl, and 900 for orthoterphenyl.

Irradiation.—At pile ambient temperature (80 ± 5°C), the benzene solutions were irradiated in a thin walled aluminium can. For lower temperatures the ampoules were contained in a welded assembly of aluminium tubes cooled by an air stream from a compressed air supply. The air was dried by passing through a 6 in. dia. × 5 ft. Pyrex flanged tube nearly filled with silica gel, and cooled by two 5/8 in. i.d. copper coils immersed in solid CO_2/trichlorethylene in one gallon vacuum flasks. The air temperatures at the exit and entry of the sample-holder were recorded.

Biphenyl and orthoterphenyl samples were irradiated at 100°C in an aluminium furnace with temperature control to ±2°C, except for one set of orthoterphenyl samples irradiated at pile ambient temperature.

All ampoules were accompanied by weighed cobalt monitors of 0·010 in. dia. wire, weight ∼ 2 mg. Thermal neutron doses ranged from $2{\cdot}05\times10^{17}$ to $7{\cdot}7\times10^{17}$ n.cm.$^{-2}$

Analysis.—The method of gas analysis has been described.[1] The " polymer " is defined as the total residue after the orginial substance has been removed by distillation. Benzene solutions after irradiation were broken open in another vessel sealed by a break-seal and transferred quantitatively *in vacuo* to a small tube which could bes ealed off. The second seal was broken with the vessel sealed to the gas line and the benzene transferred to a tared vessel by distillation. After gas analysis the small tube was sealed off and weighed with the polymer which had not been exposed to air. The tube was re-weighed after removing the polymer. Some samples of polymer were analysed for biphenyl on a high temperature gas/solid chromatography apparatus.[9] For biphenyl and orthoterphenyl about 200 mg were weighed into a thin walled tube closed at one end, 3 cm × 0·5 cm o.d. This was introduced into the closed end of another Pyrex tube opening on to a bulb which was evacuated, and sealed off after degassing the sample. The end containing the sample was heated in a heating block to 100°C for biphenyl and 170°C for orthoterphenyl until no more distilled over. The small tube was re-weighed. The distillate and residue in a representative series of samples were analysed by gas chromatography. The correction necessary to allow for the amount of the original substance left in the residue (∼ 5 % of its weight), less the amount of higher boilers in the distillate was found to be small, ∼ 2 %, and was considered negligible compared with other errors, such as variations of energy input with position in the pile.

Molecular weight determination.—This was done by ebulliometry using a multi-junction thermocouple.[10] The solvent used was chloroform or methylene chloride.

Dosimetry. Thermal neutron dose measurement.—The activity of weighed cobalt monitors, ∼2 mg of 0·010 in. dia. wire, was measured under standard conditions using a proportional counter.[11] Similar monitors had been irradiated simultaneously with gold foils, both bare and cadmium covered, the activity of the gold foils (measured on a G-M end window counter) induced by thermal neutrons having previously been related to a known thermal neutron density and time of exposure in GLEEP. These measurements gave a relation between the cobalt activity and the integrated thermal neutron exposure in BEPO. Expressed as an activation cross section the value at 2200 m/sec agrees with the literature value,[12] with a suitable correction for self-shielding in the wire. Some previously reported *G*-values [5] are too low by a factor 2790/2200 where 2790 m/sec is a measurement of the thermal neutron velocity in GLEEP, and 2200 m/sec is the velocity for which cross sections dependent on $1/v$ are quoted, due to a confusion concerning the neutron velocity for which certain flux calibrations applied. This has now been resolved.[13]

Energy deposited by the B(n,α) radiation.—The cross section for the nuclear reaction $^{10}_{5}\mathrm{B}+^{1}_{0}\mathrm{n}\rightarrow^{7}_{3}\mathrm{Li}+^{4}_{2}\alpha$ was taken as 758 barns at 2200 m/sec for natural boron.[14] The total energy was taken as 2·78 MeV, but in 93 % of the disintegrations a γ ray of energy 0·48 MeV is emitted, caused by a reversion of an excited ^{7}Li to the ground state.[15] This leaves the net heavy particle energy as 2·33 MeV. The energy deposited by the γ ray is not significant. The energy deposited by the $^{10}\mathrm{B}(\mathrm{n},\gamma)$ and $^{11}\mathrm{B}(\mathrm{n},\gamma)$ reactions is also negligible.

Energy of the pile radiation.—The background deposition of energy by pile radiation was related to the thermal neutron dose using the calorimetric calibrations of Anderson,[16] which yield the following values for the energy deposition in units of 10^4 eV g^{-1} n^{-1} cm^2: H 28·7 ± 0·8 ; C 1·77 ± 0·05; benzene 3·86 ; biphenyl 3·53 ; terphenyl 3·42.

RESULTS AND DISCUSSION

BENZENE

As with proton irradiation,[1] the −196°C gas fraction was found to be pure hydrogen and the −120°C gas fraction was found to be pure acetylene. In the region of dose studied, the yield was found to be proportional to dose. Figs. 2, 3,

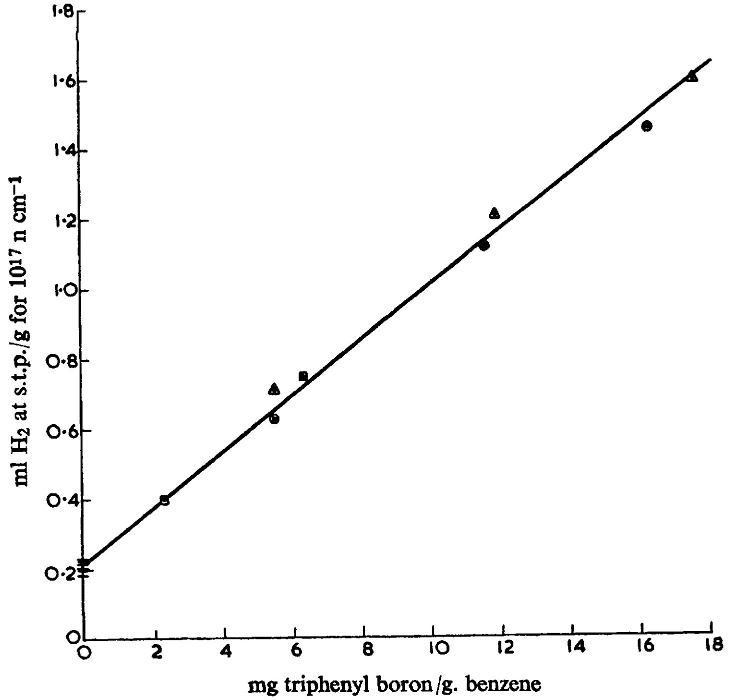

FIG. 2.—Benzene: hydrogen yield per 10^{17} n cm^{-2} against concentration of triphenyl boron. Key: △ first series, ⊙ second series, ⊡ third series, all with triphenyl boron. + No added triphenyl boron.

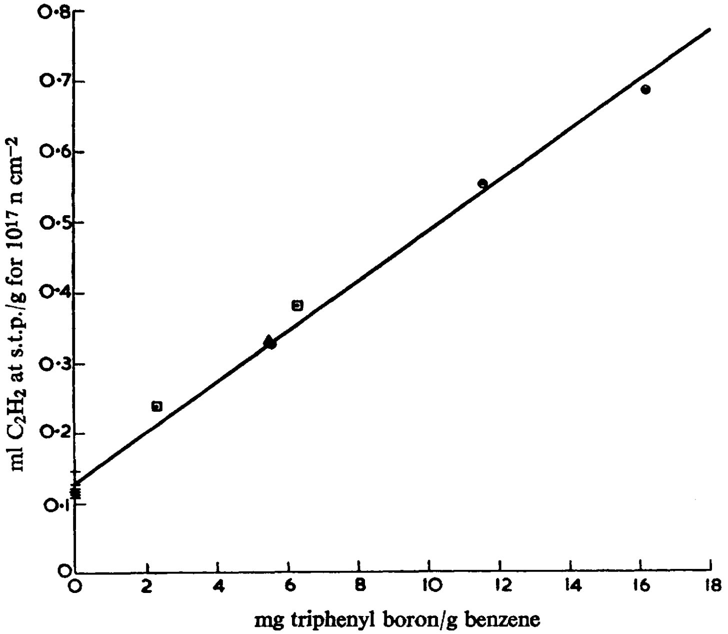

FIG. 3.—Benzene: C_2H_2 yield per 10^{17} n cm^{-2} against concentration of triphenyl boron. Key: △ first series, ⊙ second series, ⊡ third series, all with triphenyl boron. + No added triphenyl boron.

and 4 show the yields per g per 10^{17} n cm^{-2} of hydrogen, acetylene, and polymer, from the neutron irradiation of solutions of triphenyl boron, as a function of boron concentration. These results relate to pile ambient temperature (80±5°C). The linearity of these plots is evidence that the effects of the radiations involved are additive.

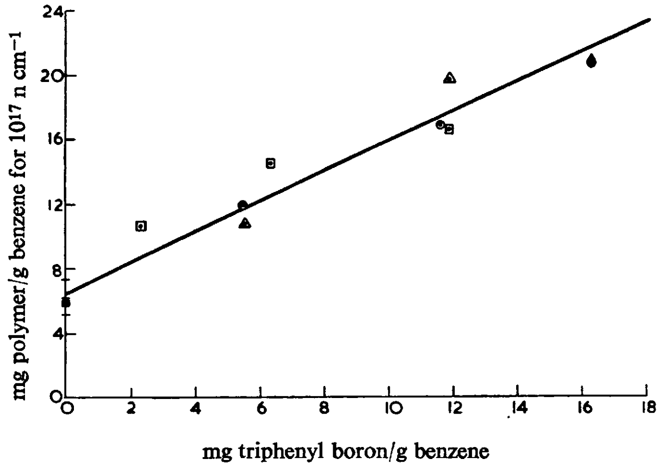

FIG. 4.—Benzene: " Polymer " yield per 10^{17} n cm^{-2} against concentration of triphenyl boron. Key: △ first series, ⊙ second series, ⊡ third series, all with triphenyl boron. + No added triphenyl boron.

From the intercepts of these graphs at zero boron concentration the *G*-values for the pile radiation were obtained using the calorimetric data. The slopes were used in conjunction with the constants of the nuclear reaction (cross-section and energy) to determine the *G*-values for the B(n, α) radiation. These *G*-values (table 1) do not depend on the calorimetry.

TABLE 1.—BENZENE WITH BORON COMPOUNDS *G* VALUES WITH STANDARD DEVIATION σ

boron compound	P		N		N		N		N	
no. of runs	13		5		6		6		5	
temp. (°C)	80		80		60		40		25	
	G	σ	*G*	σ	*G*	σ	*G*	σ	*G*	σ
pile radiation										
$G(H_2)$	0·15	0·01	0·18	0·01	0·14	0·03	0·13	0·02	0·17	0·003
$G(C_2H_2)$	0·092	0·008	0·098	0·004	0·083	0·003	0·071	0·009	0·077	0·009
$G(-C_6H_6)$	1·28	0·08	1·16	0·21	1·24	0·07	0·80	0·11	1·29	0·11
B(n,α) radiation										
$G(H_2)$	0·62	0·01	0·58	0·03	0·55	0·06	0·56	0·02	0·51	0·01
$G(C_2H_2)$	0·26	0·01	0·25	0·01	0·20	0·01	0·22	0·01	0·25	0·02
$G(-C_6H_6)$	2·13	0·12	2·56	0·48	2·22	0·16	2·28	0·12	2·10	0·29

P = triphenyl boron. N = tri-α-naphthyl boron.

DEPENDENCE ON TEMPERATURE

The other results of table 1 refer to experiments with solutions of tri-α-naphthyl boron, using smaller numbers of samples, carried out to find the variation of *G* values with temperature. Student's *t*-test[17] was applied to see if *G* values at the lower temperatures were significantly different from those at 80°C, and the gas *G* values in general were found to show significant differences, but not those for the polymer. The hydrogen G values for both pile, and B(n,α) radiation showed a consistent upward trend with a small positive temperature coefficient of 0·18 % per °C of the value at 25°C, and the acetylene value for pile radiation rose by 0·55 % per °C. The acetylene G value for the B(n,α) radiation showed no consistent trend with rising temperature. Applying the temperature coefficients, where applicable, to the G values obtained with the larger number of samples at 80°C, the final G values at 25°C are, for the B(n, α) radiation, $G(\mathrm{H_2})$ = 0·57, $G(\mathrm{C_2H_2})$ = 0·26, $G(-\mathrm{C_6H_6})$ = 2·1 and for the pile radiation $G(\mathrm{H_2})$ = 0·14, $G(\mathrm{C_2H_2})$ = 0·070, $G(-\mathrm{C_6H_6})$ = 1·3.

Table 2 shows G values obtained using 1 MeV electrons from a Van de Graaff generator and ^{60}Co and fission decay γ-radiation.

TABLE 2

radiation	no. of runs	dose W hr/g	dose rate(w/g)	temp. (°C)	conc. of boron compound (mg/g)	$G(\mathrm{H_2})$	$G(\mathrm{C_2H_2})$	$G(-\mathrm{C_6H_6})$
e	2	0·7	2	25	0	0·039	0·019	0·88
e	1	0·7	2	25	8P	0·043	0·021	—
e	2	1·0	2	25	0	0·040	0·017	0·93
e	5	1·8	2	25	0	0·041	0·021	0·81
^{60}Co-γ	5	0·31	10^{-3}	35	0	0·038	0·020	0·99
^{60}Co-γ	2	0·31	10^{-3}	35	3·5 and 16P	0·039	0·015	0·93
^{60}Co-γ	1	0·42	2×10^{-4}	35	0	0·039	0·020	1·10
^{60}Co-γ	2	0·60	10^{-3}	35	0	0·039	0·020	0·95
f.d.-γ	2	1·20	2×10^{-3}	75	0	0·040	0·024	0·90
f.d.-γ	2	1·20	2×10^{-3}	75	9N	0·039	0·019	0·92
f.d.-γ	2	1·62	2×10^{-3}	35	0	0·040	0·016	0·78
f.d.-γ	2	1·62	2×10^{-3}	35	9N	0·039	0·014	0·81

e = 1 MeV electrons.
f.d.-γ = fission decay gammas from spent fuel rods.
P = triphenyl boron.
N = tri-α-naphthyl boron.

The dose measurement for the former was by charge input, with suitable window corrections,[18] and for the latter by the use of the Fricke dosimeter (in 0·8 N $\mathrm{H_2SO_4}$) taking $G(\mathrm{Fe^{+++}})$ = 15·6. Mean values for comparison with those for the other radiations are:

1 MeV electrons $G(\mathrm{H_2})$ = 0·040, $G(\mathrm{C_2H_2})$ = 0·020, $G(-\mathrm{C_6H_6})$ = 0·85
γ-rays (35°C) $G(\mathrm{H_2})$ = 0·039, $G(\mathrm{C_2H_2})$ = 0·019, $G(-\mathrm{C_6H_6})$ = 0·94
γ-rays (75°C) $G(\mathrm{H_2})$ = 0·040, $G(\mathrm{C_2H_2})$ = 0·024, $G(-\mathrm{C_6H_6})$ = 0·90

Samples containing boron compounds have been omitted in calculating these mean values, although their effect on G values appears to be small. There does seem to be a small difference between $G(-\mathrm{C_6H_6})$ for fast electrons and γ-rays, perhaps attributable to the difference in dose rate ($\sim$2 w/g for fast electrons, $\sim10^{-3}$ w/g for γ-rays). An important feature of table 2 is the small effect of the wide variation in dose-rate. The G values at about room temperature agree with published data,[19] and the effect of temperature again is small.

The small effect of temperature on product yields with both lightly and heavily ionizing radiation suggests that no reaction with an appreciable activation energy is involved in the formation of the active intermediates, or in their competing reactions which form the basis of the effect of LET. This seems to rule out the formation of hydrogen by the combination of thermal hydrogen atoms, in competition with their addition to benzene, since the latter reaction (in the gas phase) has a collision efficiency[20] of 10^{-4}, and therefore an activation energy probably appreciably greater than that effective for the diffusion of hydrogen atoms in benzene. The result seems consistent with the formation of products (or product-forming radicals) by the interaction of excited molecules in competition, in some cases with their deactivation. The acetylene yields were less accurately measurable than the hydrogen yields and did not vary as consistently, but at all temperatures they were roughly half the hydrogen yields, indicating similar mechanisms for hydrogen and acetylene formation. The effect of increased temperature on the diffusion constant of the excited molecules will be to cause less reaction together because of the increased probability of diffusing from the zones of high concentration, but this will be offset by the increase in the rate constant for their interaction, which will be at least that of a diffusion controlled process. Other factors making for an overall small positive temperature coefficient would be a small positive dependence of the initial formation of the intermediates, or a small negative effect on the deactivation reaction.

DEPENDENCE ON LET

The gas G values show a remarkable increase above those for electron irradiation. Similar large increases in $G(H_2)$ and $G(C_2H_2)$ have been found in work with α-particles.[21] The competition of the reactions:

$$B^* + B^* \rightarrow H_2 + \text{radicals or stable products} \qquad (1)$$

$$B^* + B^* \rightarrow nC_2H_2 + \text{radicals or stable products} \qquad (2)$$

$$B^* + B \rightarrow 2\,B \qquad (3)$$

as proposed for the proton case,[1] is a likely explanation.

Schuler has found[22] the proportions of H_2, HD, D_2, evolved from 1 : 1 mixtures of benzene and benzene-d_6 were experimentally constant at 52 % : 34 % : 14 % over the range of He^{++} ion energies from 37 to 6 MeV. These proportions are essentially the same as found for fast electrons.[22] Since the heavy particle irradiations gave ~ ten times the $G(H_2)$, compared with fast electrons, it seems that unimolecular decomposition is unimportant.

The relative increase of the polymer yield with radiation type is not so large as that of the gas yields, though the absolute increase is larger than the increase in $G(H_2) + G(C_2H_2)$ by only a small factor. Thus the increase in polymer G value may possibly be accounted for in the subsequent reactions[1] of the radicals remaining after the formation of gas molecules, but the possibility of an inherent LET effect such as that suggested below for biphenyl and orthoterphenyl is not precluded.

The approximate constancy of the proportion of biphenyl in the polymer which was 23·2 % with a standard deviation of 4·3 %, as the LET and $G(-C_6H_6)$ varies, may be due to the probability of the ultimate formation of biphenyl in the most LET dependent reactions (1) and (2), and the other reactions causing polymer formation,[1] e.g.

$$B^{\ddagger} + B^{\ddagger} \rightarrow \text{radicals or stable product} \qquad (4)$$

being roughly equal. The measurements of mean molecular weight for different kinds of radiation, given in fig. 5 show an increase with dose, but no obvious correlation with radiation type, again suggesting a similarity of heavy product distribution for the different mechanisms of polymer formation.

BIPHENYL AND ORTHO-TERPHENYL

The −196°C gas fraction was found to be pure hydrogen. (Yields of −120°C fractions were about 1/10 $G(H_2)$ and were not accurately measurable.)

The results are presented in tables 3 and 4, in which G values obtained with tri-α-naphthyl boron and triphenyl boron show fair agreement for biphenyl, and good agreement for orthoterphenyl. For comparison, the initial G values at 100°C for biphenyl and orthoterphenyl for 1 MeV electrons, determined by a method already described,[18] are $G(H_2) = 0{\cdot}0092$, $G(-M) = 0{\cdot}26$ for biphenyl, and $G(H_2) = 0{\cdot}0054$, $G(-M) = 0{\cdot}11$ for orthoterphenyl. The increase in gas G values with LET may be attributed, by analogy, to a mechanism similar to that proposed for benzene:

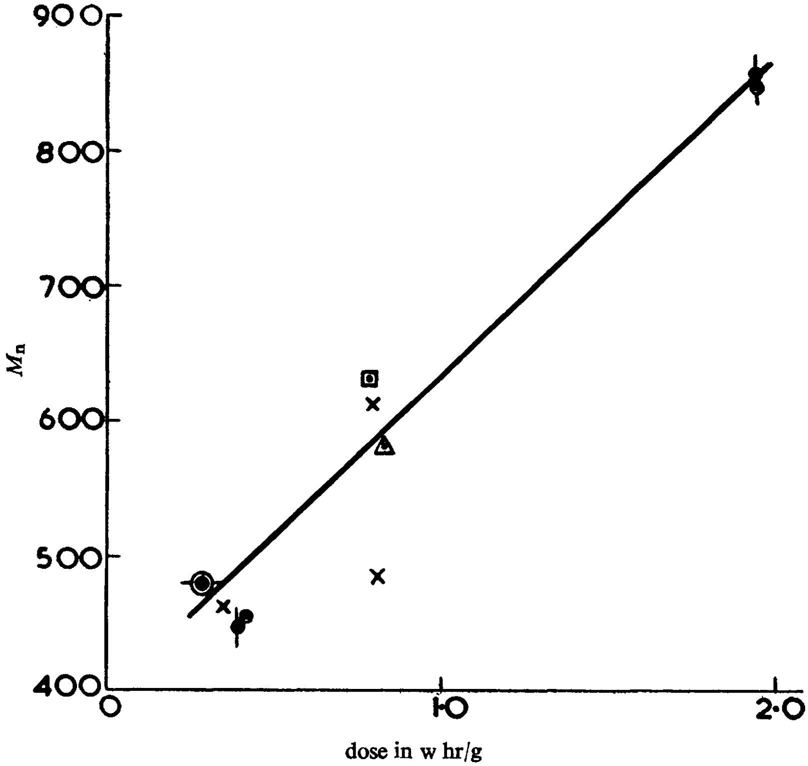

FIG. 5.—Mean molecular weight of benzene " polymer " against dose.

⊙ ^{60}Co γ radiation 5900 rad/min.
—⊙— ^{60}Co γ radiation 1540 rad/min.
× 1 MeV protons.
I⊙I fast electrons.
⊡ BEPO pile radiation.
△ B(n,α) radiation.

$$M^* + M^* \rightarrow H_2 + \text{radicals or stable products} \qquad (5)$$

$$M^* + M \rightarrow 2M \qquad (6)$$

The observation of Burr[23] that the proportions of H_2, HD, and D_2 evolved on the γ irradiation of a mixture of biphenyl and biphenyl-d_{10} were the same for the liquid and the solid, is consistent with this mechanism.

The increases in polymer *G* values with LET are so large that although some of the increases may be due to the larger numbers of radicals arising from reaction (5) at higher LET, another mechanism must be operative. It is possible that radicals which lead to polymer formation may be formed in interactions of excited molecules which do not produce gas molecules.

$$M^{\ddagger} + M^{\ddagger} \rightarrow \text{radicals or stable products} \tag{7}$$

$$M^{\ddagger} + M \rightarrow 2M \tag{8}$$

the deactivation reaction providing the first order competition necessary for an LET dependence. The radicals formed in reaction (7), such as $\cdot C_{12}H_9$ and $\cdot C_{12}H_{11}$ from biphenyl would be expected to add to the surrounding substrate molecules to form larger radicals,[24] and finally radicals would react together in combination or disproportionation reactions. If the excited molecules involved in this reaction were envisaged as triplet states, then in addition to reaction (7) the well-known bimolecular quenching with spin reversal must occur.[25] The participation of a reaction analogous to reaction (7) has been observed in the flash photolysis of aqueous solutions of fluorescein and eosin.[26] The interaction of two triplet states produces radicals of an oxidised and a reduced form of the dye molecule; the spectra of the radicals were observed in these favourable circumstances, where their lifetimes were greater than that of the triplet state. Burr [27] has reported values of $G(-M)$ for orthoterphenyl, using $^{210}P_0$ α radiation, from 0·4 at 30°C to 0·9 at 300°C, with a linear dependence of log $G(-M)$ against 1/T°K. The interpolated value of $G(-M)$ at 100°C is 0·53 approx. This value is higher than the electron *G*-value, but absolutely seems rather low, since the radiation transmitted from the retaining foil would be expected to have an LET near that of the *B*(n,α) radiation. The small overall activation energy found in this work is not inconsistent with the mechanism proposed above.

TABLE 3.—BIPHENYL WITH BORON COMPOUNDS *G* VALUES WITH STANDARD DEVIATIONS

boron compound	P		N		P and N combined	
no. of runs	4		8		12	
temp., °C	100		100		100	
	G	σ	*G*	σ	*G*	σ
pile radiation						
$G(H_2)$	0·060	0·009	0·062	0·005	0·059	0·005
$G(-C_{12}H_{10})$	0·64	0·07	0·73	0·03	0·69	0·03
^{10}B (n,α) radiation						
$G(H_2)$	0·18	0·02	0·16	0·01	0·17	0·01
$G(-C_{12}H_{10})$	1·59	0·10	1·46	0·07	1·52	0·05

P = triphenyl boron. N = tri-α-naphthyl boron.

TABLE 4.—O-TERPHENYL WITH BORON COMPOUNDS *G* VALUES WITH STANDARD DEVIATIONS

boron compound	P		N		P and N combined	
no. of runs	4		8		12	
temp. (°C)	80		100		80-100	
	G	σ	*G*	σ	*G*	σ
pile radiation						
$G(H_2)$	0·050	0·005	0·045	0·002	0·042	0·002
$G(-C_{18}H_{14})$	0·39	0·04	0·39	0·02	0·43	0·02
^{10}B (n,α) radiation						
$G(H_2)$	0·19	0·004	0·17	0·004	0·19	0·002
$G(-C_{18}H_{14})$	0·91	0·03	1·11	0·05	0·93	0·02

P = triphenyl boron. N = tri-α-naphthyl boron.

The greater dependence of gas yields on LET may be due to the greater relative increase in the ratio of the rates of reactions (5) and (6), compared with that of (7) and (8). Some excited molecules may react directly with polymer or radicals already formed providing a part of the polymer yield independent of LET.

It has been suggested that a clue in explaining the effects of LET may be in radical combinations in the track spurs.[28] The importance of radicals in determining the major part of the product distribution cannot be denied. Work in this laboratory and elsewhere has shown parallels in the radiolytic products and those formed by the attack of radicals generated otherwise than by radiation, both with biphenyl [29, 30] and toluene.[28]

However it is debatable whether the non-dependence of a bimolecular product yield (viz. phenyl tolyl methanes in the radiolysis of toluene), on iodine concentration [28] is good evidence for an inter-radical spur reaction, especially when the dimerisation of one of the radicals, benzyl, showed an appreciable dependence. The well known dependence of the molecular G values on scavenger concentration in aqueous radiation chemistry,[31] which may be taken as a prototype for radical spur reactions, shows that the track spur is not impenetrable. If as an alternative to intercombination, the fate of radicals is considered to be reaction with the substrate, and the formation of radicals is not dependent on LET, then a simple model based on radical reactions alone would predict a decrease in $G(-M)$ with increasing LET. The lack of dependence on scavenger concentration and the increase of $G(-M)$ with increasing LET may both be the result of excited molecule interactions in the track spurs. If inter-radical spur reactions do occur it is difficult to see how they are relevant to this dependence of $G(-M)$.

One important difference between radiation effects in aromatic and aqueous systems lies in the ability of the substrate molecules to react quickly with radicals in the former case. Another lies in the inherent stability of the excited molecule and the parent positive ion with respect to decomposition.[32] With U.V. light of wavelengths 1860 and 1935 Å, liquid water in the presence of scavengers decomposes to H atoms and OH radicals with a quantum yield of $\sim 1{\cdot}0$ (see ref. 33). Attempts to photolyse benzene vapour,[34] and liquid,[35] show very low quantum yields of hydrogen, (e.g. for the vapour $\sim 3 \times 10^{-3}$). This may be due to the efficacy of radical and atom scavenging by the benzene, which would also account for the lack of exchange with added D_2. An additional cause may be the low probability of the reaction [33]

$$\text{Ar H} \rightarrow \cdot\text{Ar} + \text{H}. \tag{9}$$

Burton and Chang [36] have discussed the radiation chemistry of benzene and concluded that " explanations based on interception of radicals by benzene appear to be inadequate to account entirely for the low yields ". A difficulty in the use of radical scavengers in organic systems to find the efficiency of reactions such as (9) is their ability to react with excited molecules, or radicals precursors [37, 38] so that a true radical count may not be obtained. However the outstanding experimental feature in the decomposition of these aromatic substances is that the total decomposition $G(-M)$ is markedly dependent on LET, an effect not found with water, where the proportions of radical and molecular yields show large variations, but not $G(-H_2O)$ either net or gross.

This feature of aromatic substances cannot be explained on the basis of a break-up into radicals governed by the energy input, followed by radical reactions governed by the resulting concentrations. The mechanism we have used to explain the effect of LET is based on the stability of the single aromatic molecule to primary decomposition. It requires the interaction of excited states to produce decomposition. The

LET effect is then due to the concentrations of excited molecules, the radical precursors, although the formation of the ultimate products is mainly by the reactions of radicals.

Our thanks are due to Mr. T. H. Bates, who did the molecular weight measurements, to Mr. B. E. Cooper for assistance with statistical analysis, to Mr. T. F. Williams for advice, and to Dr. W. Wild for helpful discussions.

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