

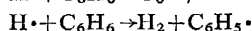
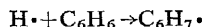
# $\gamma$ -Radiolysis of Benzene at High Temperatures and Pressures

BY W. G. BURNS AND W. R. MARSH

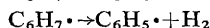
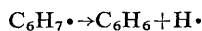
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Benzene was irradiated at 260–390°C, and yields of hydrogen, methane, acetylene, ethylene, ethane, biphenyl and conversion to polymer were measured as functions of dose, density and temperature. No special phenomena were observed at or near the critical temperature. In general, all yields decreased smoothly with increasing density, and increased with increasing temperature. The most marked increase with temperature was in  $G(\text{H}_2)$  which increased approximately thirty-fold (from  $\sim 0.1$  to  $\sim 3$ ) from 260 to 390°C. The only dimer found was biphenyl whose yield was also strongly temperature dependent. The effect of density was attributed to the competition between deactivation and decomposition of excited molecules, and the effect of temperature to the competition between different reactions of hydrogen atoms, or cyclohexadienyl radicals. The competing hydrogen atom reactions considered were:



but competing modes of decomposition of the cyclohexadienyl radical



were adjudged a more probable cause of the variation of  $G(\text{H}_2)$  with temperature. Methane, ethylene, and ethane, appeared to be secondary products, and in the long irradiations necessary to measure  $G(\rightarrow\text{polymer})$  thermal reactions, such as the polymerization of acetylene, and the hydrogenation of acetylene and ethylene affected the observed yields. The effects of density and temperature on radiolytic yields were considered in relation to models which have been proposed to explain product formation in the radiolysis of aromatic liquids.

In the radiolysis of ammonia at supercritical temperatures<sup>1</sup> large decreases in  $G(\text{N}_2)$  and  $G(\text{H}_2)$  with increasing density, found below the critical density, were attributed to the effects of ion-clustering,<sup>2</sup> as were changes in product yields with density in irradiated supercritical propylene.<sup>3</sup> The effect of density on product yields in the radiolysis of n-butane<sup>4</sup> and ethane<sup>5</sup> was ascribed to the competing reactions of primary ions, such as fragmentation, deactivation, ion-molecule reactions, and neutralization. It was of interest to discover whether similar effects were observable in the radiolysis of benzene under near-critical and supercritical conditions. In addition, if competition between the interaction and deactivation of excited molecules, proposed to explain L.E.T. effects in aromatic hydrocarbons,<sup>6</sup> were effective under such conditions, increases in yields with increasing density would be expected as the result of changes in the relevant parameters. Any change in the distribution of products with temperature was also of interest with respect to the thermal spike models which have been proposed for the effects of low L.E.T. radiation,<sup>7-9</sup> and for the effects of L.E.T. on radiation yields.<sup>10</sup>

## EXPERIMENTAL

### MATERIALS AND IRRADIATION

Phillips Research Grade benzene, dried by passage through activated molecular sieve, was used throughout, and high-purity gases which were used as chromatographic standards

were obtained from the Chemical Standards Division of the National Physical Laboratory. Stainless steel pressure vessels, described elsewhere,<sup>11</sup> of volume 8.2 ml were used, and irradiations carried out on amounts of benzene in the range 0.2-4.0 g.

Short irradiations were carried out in a 1000 Ci <sup>60</sup>Co source, and longer irradiations in the T.I.G. Spent Fuel Facility. In the latter case, dosimetry was carried out both before and after experiments in order to check any variation in dose-rate which could arise due to replacement or removal of neighbouring fuel elements. Typical dose-rates were  $4 \times 10^{17}$  eV g<sup>-1</sup> min<sup>-1</sup> in the <sup>60</sup>Co source, and  $8 \times 10^{17}$  eV g<sup>-1</sup> min<sup>-1</sup> in the T.I.G. Facility.

#### DOSIMETRY

The validity of extrapolation from liquid dosimetry to gaseous systems is doubtful since the processes of energy absorption are different in the two systems. In liquids the energy absorbed arises mainly as a result of Compton interactions originating in the liquid itself, whereas in gases, particularly at low density, the energy absorbed is due to recoil electrons produced in the vessel walls. As the density increases, Compton interactions in the irradiated substance become more important. Burton<sup>1</sup> has suggested that a correction factor be applied to gaseous systems when the dosimetry is based on liquids, and we have therefore carried out dosimetry in both liquid and gas phases. The following results for the dose rate in benzene in the irradiation vessel were obtained using  $G(N_2) = 10.0$  from nitrous oxide gas,<sup>12</sup>  $G(H_2) = 0.039$  and 5.50 for liquid benzene and cyclohexane respectively at 30°C, making the conversion from dose-rate in N<sub>2</sub>O and cyclohexane to that in benzene on the basis of electron density.

dosimetric substance	N <sub>2</sub> O	N <sub>2</sub> O	N <sub>2</sub> O	N <sub>2</sub> O	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>
density g ml <sup>-1</sup>	·0025	·0105	·057	·079	·779	·879
dose rate $\times 10^{17}$ eV g <sup>-1</sup> min <sup>-1</sup>	6.18	5.96	5.42	5.36	5.13	5.00

There are few data for  $G(N_2)$  from nitrous oxide as a function of density, but our results agree reasonably with a statement<sup>13</sup> that it is independent of pressure from 1.70 bar (density 0.002-0.137 g ml<sup>-1</sup>), and with data<sup>14</sup> over the pressure range 7.36 bar (density 0.014-0.071 g ml<sup>-1</sup>) showing little variation of  $G(N_2)$ . The decrease in dose-rate with increasing density may be a real effect, or be due to a decrease in  $G(N_2)$  with density; however, over the range of the experiments (0.030-0.879 g ml<sup>-1</sup>), the variation is small and dose-rates expressed as eV g<sup>-1</sup> min<sup>-1</sup> in liquid and vapour are equal to within  $\pm 7\%$ . We have therefore used  $G(H_2) = 0.039$  from liquid benzene at 30°C as the dosimetric standard for all irradiations.

#### ANALYSIS

The products of irradiation were determined by gas chromatography. Gases non-condensable at -196°C were analyzed on a 6 mm bore, 1.5 m long, column of Molecular Sieve 5A at 30°C, using a katharometer with thermistor detectors. A further gas fraction non-condensable at -78°C was analyzed on a 6 mm bore, 4.5 m, column packed with bis-2-methoxyethyl adipate 20 : 80 on 60-80 mesh Chromosorb P maintained at -15°C, using a flame ionization detector.

Liquid products were analyzed on an F and M Model 609 chromatograph equipped with a flame ionization detector. A 6 mm bore, 1.5 m, column, packed with 5 % lithium chloride on 30-60 mesh firebrick,<sup>15</sup> was used; by temperature programming from 125 to 280°C at 18° per min, biphenyl was eluted in 8-10 min, and separated from terphenyls which were eluted in 15-20 min. Polymer yields from the longer irradiations were determined by a method described previously.<sup>16</sup>

#### RESULTS

The yields of hydrogen, acetylene, ethylene, and ethane, for a dose of  $3.6 \times 10^{20}$  eV g<sup>-1</sup> are shown in fig. 1-3 at varying density and temperature. Fig. 2 also gives biphenyl yields at low doses at varying density and temperature. Experiments at

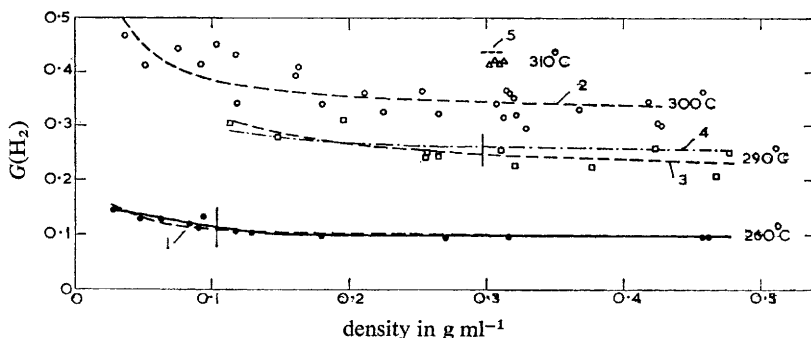


FIG. 1.— $G(\text{H}_2)$  against Density for a dose of  $3.6 \times 10^{20} \text{ eV g}^{-1}$ ,  $\bullet$ ,  $260^\circ\text{C}$ ;  $\square$ ,  $290^\circ\text{C}$ ;  $\circ$ ,  $300^\circ\text{C}$ ;  $\triangle$ ,  $310^\circ\text{C}$ . Curves 1, 2, 3,  $G(\text{H}_2)$  from eqn. [2],  $A$  and  $B$  obtained by least-squares from eqn. [3]. Curve 4,  $G(\text{H}_2)$  from [2] at  $290^\circ\text{C}$ , constants obtained by interpolation from results at  $260$  and  $300^\circ\text{C}$ . Curve 5, calculated curve at  $310^\circ\text{C}$ . The vertical line on the  $260^\circ\text{C}$  curve is the transition density from a one-phase to a two-phase system; that on the  $290^\circ\text{C}$  curve is at the critical density.

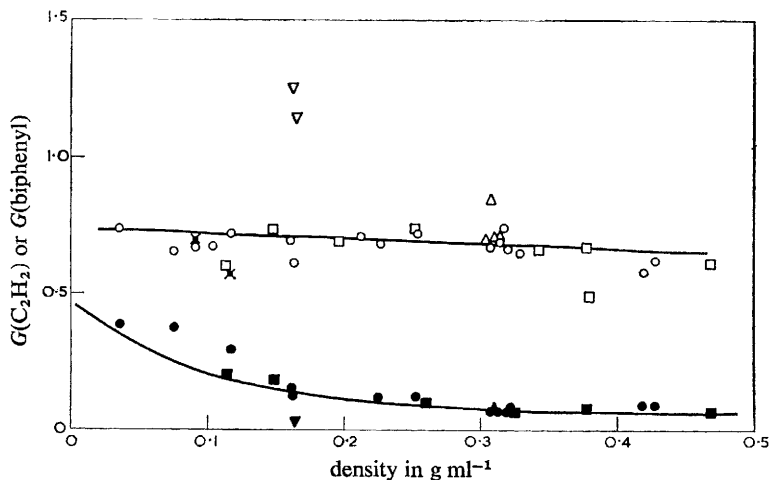


FIG. 2.— $G(\text{C}_2\text{H}_2)$  and  $G(\text{biphenyl})$  against density for a dose of  $3.6 \times 10^{20} \text{ eV g}^{-1}$ ,  $G(\text{C}_2\text{H}_2)$ :  $\blacksquare$ ,  $290^\circ\text{C}$ ;  $\bullet$ ,  $300^\circ\text{C}$ ;  $\blacktriangle$ ,  $310^\circ\text{C}$ ;  $\blacktriangledown$ ,  $350^\circ\text{C}$ . Curve is for competition between reactions (7), (8) and (9), for points at  $290$ – $310^\circ\text{C}$ .  $G(\text{biphenyl})$ :  $\times$ ,  $260^\circ\text{C}$ ;  $\square$ ,  $290^\circ\text{C}$ ;  $\circ$ ,  $300^\circ\text{C}$ ;  $\triangle$ ,  $310^\circ\text{C}$ ;  $\triangledown$ ,  $350^\circ\text{C}$ .

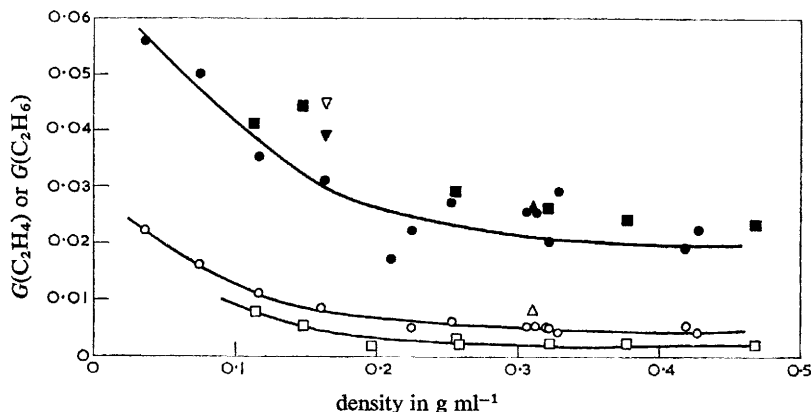
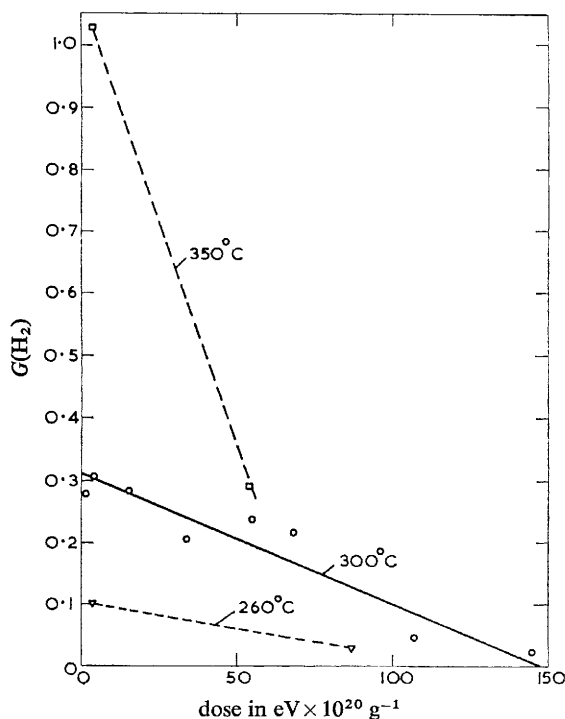


FIG. 3.— $G(\text{C}_2\text{H}_4)$  and  $G(\text{C}_2\text{H}_6)$  against density for a dose of  $3.6 \times 10^{20} \text{ eV g}^{-1}$ ,  $\blacksquare$ ,  $290^\circ\text{C}$ ;  $\bullet$ ,  $300^\circ\text{C}$ ;  $\blacktriangle$ ,  $310^\circ\text{C}$ ;  $\blacktriangledown$ ,  $350^\circ\text{C}$ .  $G(\text{C}_2\text{H}_6)$ : temperatures as for  $G(\text{C}_2\text{H}_4)$ , but with open symbols.

300°C and lower doses (table 1) showed no important effect of dose on  $G(\text{H}_2)$  and  $G(\text{biphenyl})$  up to this dose.  $G(\text{C}_2\text{H}_2)$  tends to be higher at low doses, whereas  $G(\text{C}_2\text{H}_6)$  and  $G(\text{C}_2\text{H}_4)$ , especially the latter, decrease with decreasing dose. This table also gives low dose yields at 350 and 390°C. Another series of experiments was

TABLE 1.—EFFECT OF TEMPERATURE AND DOSE ON PRODUCT YIELDS AT LOW DOSE

temp. °C	dose $\text{eV} \times 10^{20} \text{ g}^{-1}$	density $\text{g ml}^{-1}$	$G(\text{H}_2)$	$G(\text{C}_2\text{H}_2)$	$G(\text{C}_2\text{H}_4)$	$G(\text{C}_2\text{H}_6)$	$G(\text{biphenyl})$
300	3.60	0.161	0.394	0.148	0.040	0.0073	0.69
300	1.25	0.162	0.378	—	0.036	—	0.67
300	0.54	0.167	0.400	0.208	0.020	0.006	0.77
350	2.97	0.165	1.12	0.017	0.046	0.054	1.14
350	2.83	0.163	1.05	0.025	0.044	0.061	1.25
350	3.61	0.163	1.03	—	0.039	0.045	1.53
390	3.03	0.165	3.19	0.00	0.00	0.124	3.63
390	3.08	0.161	2.47	0.00	0.00	0.112	3.49
390	2.95	0.161	2.89	0.01	0.00	0.114	3.70

FIG. 4.— $G(\text{H}_2)$  against dose at density  $0.21 \text{ g ml}^{-1}$ ,  $\nabla$ , 260°C;  $\circ$ , 300°C;  $\square$ , 350°C.

carried out at higher doses in order to measure reasonably accurately the conversion of benzene to polymer. In this series, the yields of biphenyl, methane, and the above gases were also measured. For a constant density of  $0.21 \text{ g ml}^{-1}$  the effects of dose and temperature on  $G(\text{H}_2)$  are shown in fig. 4, of dose on  $G(\text{CH}_4)$ ,  $G(\text{C}_2\text{H}_2)$ ,  $G(\text{C}_2\text{H}_4)$  and  $G(\text{C}_2\text{H}_6)$  in fig. 5, and on  $G(\text{biphenyl})$  and  $G(\rightarrow\text{polymer})$  in fig. 6. At a constant high dose of  $145 \times 10^{20} \text{ eV g}^{-1}$ , the effect of density on  $G(\text{CH}_4)$ ,  $G(\text{C}_2\text{H}_4)$ ,  $G(\text{C}_2\text{H}_6)$ ,

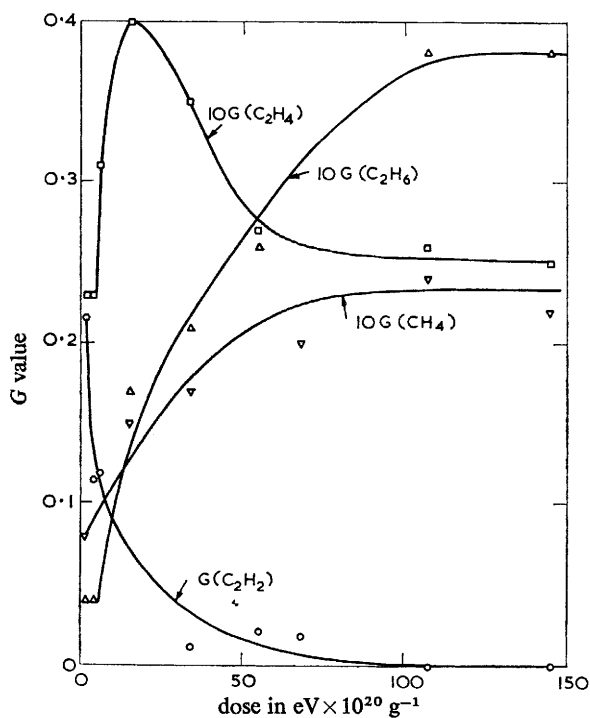


FIG. 5.—Product  $G$  values against dose at density  $0.21 \text{ g ml}^{-1}$ ,  $300^\circ\text{C}$ .  $\circ$ ,  $G(\text{C}_2\text{H}_2)$ ;  $\nabla$ ,  $10 G(\text{CH}_4)$ ;  $\Delta$ ,  $10 G(\text{C}_2\text{H}_6)$ ;  $\square$ ,  $10 G(\text{C}_2\text{H}_4)$ .

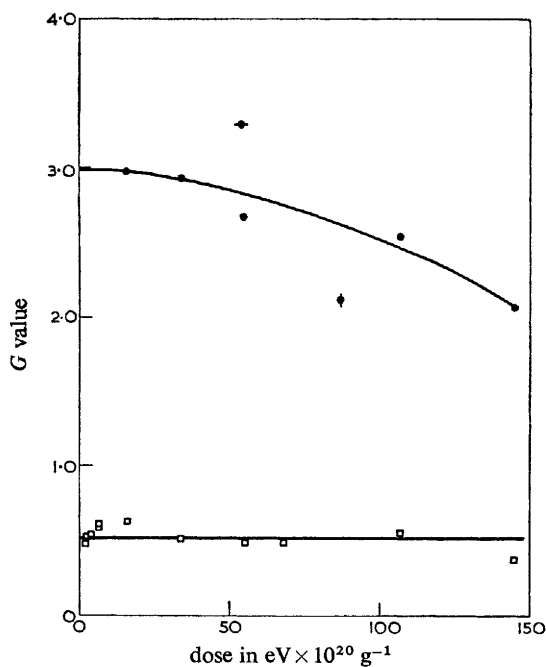


FIG. 6.— $G(\rightarrow\text{polymer})$  and  $G(\text{biphenyl})$  against dose at density  $0.21 \text{ g ml}^{-1}$ .  $\bullet$ ,  $G(\rightarrow\text{polymer})$  at  $300^\circ\text{C}$ ;  $\blacklozenge$ ,  $G(\rightarrow\text{polymer})$  at  $260^\circ\text{C}$ ;  $\bullet$ ,  $G(\rightarrow\text{polymer})$  at  $350^\circ\text{C}$ ;  $\square$ ,  $G(\text{biphenyl})$  at  $300^\circ\text{C}$ .

$G(\text{biphenyl})$ , and  $G(\rightarrow\text{polymer})$  is shown in fig. 7. The dependence on temperature of the rate constant  $k_{th}$  for thermal decomposition to hydrogen, expressed as first-order for the reaction  $\text{C}_6\text{H}_6 \rightarrow \text{H}_2 + \text{products}$ , is shown in fig. 8 as a plot of  $\log_{10} k_{th}$

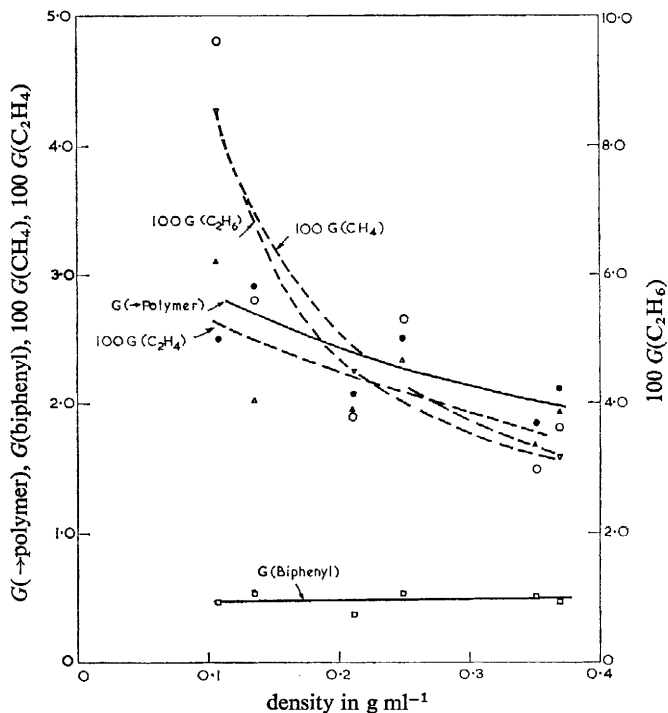


FIG. 7.—Product  $G$  values against density at a dose of  $1.45 \times 10^{22} \text{ eV g}^{-1}$  at  $300^\circ\text{C}$ . ●,  $G(\rightarrow\text{polymer})$ ; □,  $G(\text{biphenyl})$ ; △,  $100 G(\text{C}_2\text{H}_4)$ ; ▽,  $100 G(\text{CH}_4)$ ; ○,  $100 G(\text{C}_2\text{H}_6)$ .

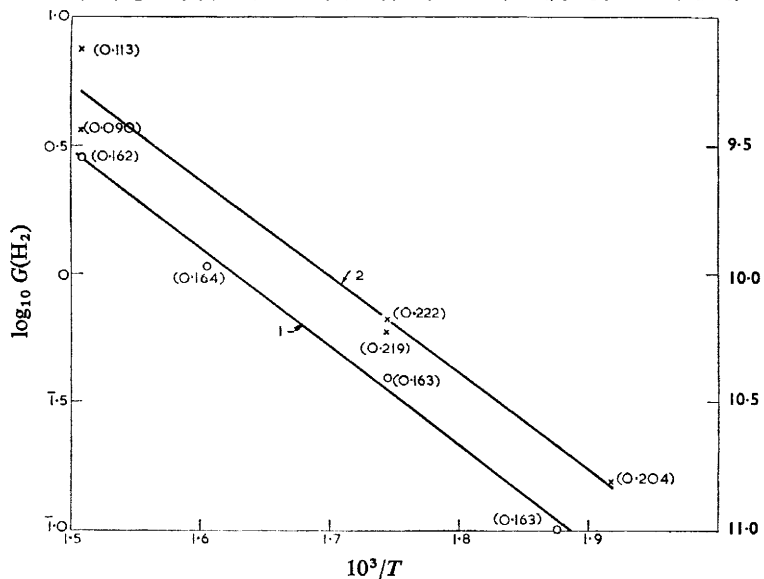


FIG. 8.— $-\log_{10} G(\text{H}_2)$  and  $\log_{10} k_{th}$  against  $1/T$ . ○,  $\log_{10} G(\text{H}_2)$ ; ×,  $\log_{10} k_{th}$ . Line 1, least-squares line giving  $G = 1.80 \times 10^6 \exp(-8,900/T)$ . Line 2, least squares line giving  $k_{th} = 2.48 \times 10^{-4} \exp(-8,600/T) \text{ sec}^{-1}$ . Numbers in brackets are densities in  $\text{g ml}^{-1}$ .

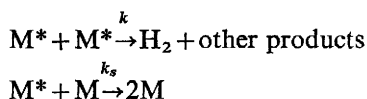
against  $1/T$ , where  $T$  is the absolute temperature. The maximum amount of purely thermal decomposition, estimated from hydrogen production, is less than 2 % of the total effect of radiation at the experimental temperature.

## DISCUSSION

### HYDROGEN YIELDS

Fig. 1 shows that  $G(\text{H}_2)$  at low doses is not sensitive to changes in density at and near the critical temperature ( $290^\circ\text{C}$ ), changing only from 0.3 to 0.45 as the density decreases from 0.426 to 0.037 g ml<sup>-1</sup> at  $300^\circ\text{C}$ . However, fig. 8 shows a marked influence of temperature, with an apparent overall activation energy similar to that in the purely thermal decomposition. We now discuss various possible mechanisms for the formation of hydrogen and the variation of its yield with density and temperature.

INTERACTION OF EXCITED SPECIES SUBJECT TO DEACTIVATION.—If the mechanism suggested for the room temperature decomposition,<sup>6, 17</sup>



were operative at  $300^\circ\text{C}$ ,  $G(\text{H}_2)$  would be much lower, and would increase with increasing density. Calculations were made of  $G(\text{H}_2)$  based on reasonable assumptions regarding the temperature and density variation of the relevant parameters, which give the observed values of  $G(\text{H}_2)$  at room temperature for this mechanism. The assumptions made were as follows. The diffusion constant  $D$  was assumed to be related to the viscosity  $\eta$  by the equation<sup>18</sup>  $kT/D\pi r'\eta = 3.69$ , where  $r'$  for benzene is taken<sup>18</sup> as 0.275 nm,  $\eta$  at the critical density was obtained from the data of Heiks and Orban,<sup>19</sup> and  $D$  was assumed inversely proportional to the square root of the density  $\rho$  at the critical temperature. The diffusion-controlled rate constant  $k$  was assumed proportional to  $D$ ; the rate constant  $k_s$ , assumed to be related to collisional deactivation, was taken to be proportional to  $T^{\frac{1}{2}}$ , and the concentration  $c_s$  of deactivating molecules was taken as proportional to density. The spur radius, since it is related to the range of a "typical" secondary electron, was assumed inversely proportional to the density. Low  $G$  values from 0.013 to 0.114 were found for densities 0.1 to 0.5 g ml<sup>-1</sup> at  $290^\circ$ , showing that the effect of temperature has caused this mechanism to be inapplicable or to account for only a small part of  $G(\text{H})_2$  under these conditions.

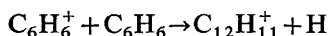
EFFECT OF PRESSURE ON RATE CONSTANTS.—The observed decrease in  $G(\text{H}_2)$  with increasing pressure is in the correct sense for a dependence due to an increase in volume of activation, which would be expected to occur in any mechanism involving bond dissociation,<sup>20</sup> e.g., of an excited molecule. However, the decrease is observed for such small changes in pressure (a few tens of bars) compared with those for which this kind of mechanism is normally postulated,<sup>20</sup> and would need such a large change in volume of activation (a few hundred ml per mole at  $0^\circ\text{C}$ ) that other mechanisms are more probable.

ION CLUSTERING.<sup>2</sup>—There appear to be no abrupt changes with density, at or below the critical density, which could be ascribed to changes in the make-up of ion clusters.

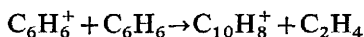
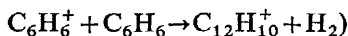
COMPETITION BETWEEN EXCITED-ION FRAGMENTATION AND DEACTIVATION.—Calculations by Stevenson<sup>21</sup> suggest that the competition between fragmentation and deactivation of parent ions cannot be the cause of the decrease of  $G(\text{H}_2)$  with increasing density. He concluded that in 0.1 ns (the approximate interval between collisions

of a single molecule at S.T.P.) after formation, no fragmentation of benzene parent ions occurs. In all experiments reported here the time between collisions will be less than 0.1 ns, so that the initial excited ions should be stabilized against fragmentation.

COMPETITION BETWEEN ION-MOLECULE REACTIONS AND ION NEUTRALIZATION.—If the former of these two reactions gives rise to hydrogen and the latter does not, their competition is a possible cause of the dependence of  $G(\text{H}_2)$  on density. El Komoss and Magee<sup>22</sup> have shown that for some simple molecules there is a suitable dependence on density of the fraction of electrons recaptured, and early work at low pressures ( $\sim 0.1 \text{ Nm}^{-2}$ ) has demonstrated the occurrence of the following ion-molecule reactions:<sup>23</sup>

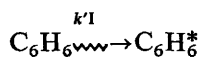


(or possibly,



However, recent work on the reactions of  $\text{C}_6\text{H}_6^+$  with benzene at higher pressures<sup>24</sup>  $\sim 100 \text{ Nm}^{-2}$  shows that the parent ion  $\text{C}_6\text{H}_6^+$  reacts very slowly with benzene, so that this mechanism is unlikely.

COMPETITION BETWEEN EXCITED MOLECULE DECOMPOSITION AND DEACTIVATION.—We will need to refer to the following reactions



If the decomposition reaction (1) were to lead to a constant fraction  $f$  of hydrogen molecules for each decomposition,  $G(\text{H}_2)$  would be given by

$$G(\text{H}_2) = G(\text{C}_6\text{H}_6^*)fk_1/\{k_1 + k_2[\text{C}_6\text{H}_6] + k_{2a}\},$$

which is of the requisite form for the observed density dependence. A plot of  $1/G(\text{H}_2)$  against density for results at 300°C yields a straight line with intercept  $(k_1 + k_{2a})/k_1fG(\text{C}_6\text{H}_6^*) = 2.22 \pm 0.064$ , and slope  $k_2/k_1fG(\text{C}_2\text{H}_6) = 2.45 \pm 0.24 \text{ ml g}^{-1}$ , so that if  $k_{2a} = 0$ ,  $fG(\text{C}_6\text{H}_6^*) = (2.22)^{-1} = 0.451$ , and  $k_2/k_1 = 1.10 \text{ ml g}^{-1} = 0.086 \text{ l mole}^{-1}$ ; at 260°C  $fG(\text{C}_6\text{H}_6^*) = 0.130$  and  $k_2/k_1 = 0.91 \text{ ml g}^{-1}$ . Fig. 9 shows curves of  $G(\text{H}_2)$  against density calculated from the above equation using these constants. This equation is equivalent to [4], used later.

#### ALTERNATIVE FATES OF HYDROGEN ATOMS OR RADICALS

(i) The large temperature effect in  $fG(\text{C}_6\text{H}_6^*)$  might arise if the alternative reactions of the hydrogen atoms, reaction (3) abstraction from, and reaction (4), addition to, benzene, possess different activation energies, the former, with the higher activation energy, not being significant at normal temperatures. James and Suart<sup>25</sup> have



shown that although the resonance energy of the cyclohexadienyl radical is sufficient to suppress its addition and abstraction reactions in cyclohexane vapour up to 200°C, the decomposition reaction (5) is important at 136–180°C in the vapour phase. This decomposition, if it were the predominant fate of the  $C_6H_7\cdot$  radical in the temperature range 200–400°C and at our pressures, would prevent the competition between (3) and (4), since (4) would no longer effectively remove hydrogen atoms. For the competition to be effective we must postulate that under our experimental conditions the rate

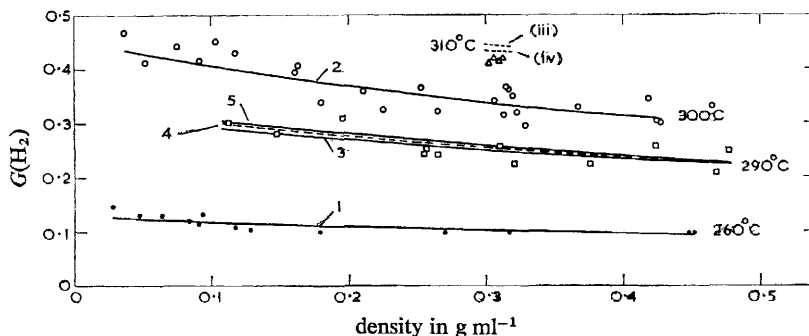


FIG. 9.— $G(H_2)$  against density for a dose of  $2.6 \times 10^{20}$  eV  $g^{-1}$ . Points are as for fig. 1. Curves 1, 2, 3 are from eqn. [4], with  $G^1$  and  $S$  obtained by least-squares from plots of  $1/G(H_2)$  against density. Curves 4 and 5 are with constants obtained at 290° from those at 260 and 300°C by methods (iii) and (iv) respectively. Curves (iii) and (iv) are those predicted at 310° from the points at 260 and 300° by methods (iii) and (iv).

of reaction of the cyclohexadienyl radical with surrounding molecules (6), is comparable with its rate of decomposition by (5). A steady-state treatment of reactions (1) to (6) yields the expression

$$G(H_2) = G(C_6H_6^*) / \{ (1 + D + Cx) [1 + ABx / (1 + Bx)] \}, \quad [1]$$

where  $x = [C_6H_6]$ ,  $C = k_2/k_1$ ,  $A = k_4/k_3$ ,  $B = k_6/k_5$ ,  $D = k_{2a}/k_1$ . The expression shows that there can be a dependence on density due to the competition between reactions (4) and (3), (6) and (5), even if  $C \simeq 0$ , i.e.,  $k_1 \gg k_2$ ; it also predicts a variation of  $G(H_2)$  with temperature. If we assume that decomposition is the predominant fate of  $C_6H_6^*$ , i.e.,  $(D + Cx) \ll 1$ , eqn. [1] simplifies to

$$G(H_2) = G(C_6H_6^*) / [1 + ABx / (1 + Bx)]. \quad [2]$$

Rearrangement gives

$$\left\{ \frac{G^*}{G(H_2)} - 1 \right\}^{-1} = \frac{1}{ABx} + \frac{1}{A} \quad [3]$$

where  $G^* = G(C_6H_6^*)$ ; using a chosen value for  $G^*$ , the left-hand side of this equation can be calculated for each value of  $G(H_2)$ , and  $A$  and  $B$  obtained from the linear plot against  $1/x$ .  $A$  and  $B$  were so derived from a least-squares treatment of [3] at 260 and 300°, and expressed as  $A_0 \exp(-E_A/RT)$  and  $B_0 \exp(-E_B/RT)$ . Values of  $A_0$ ,  $B_0$ ,  $E_A$ ,  $E_B$  and of  $G(H_2)$  at density 0.163 g  $ml^{-1}$  at 350 and 390° derived from these constants and eqn. [2] are given in table 2.

The dependence of  $G(H_2)$  on density at 290° was also calculated from these constants and is given in fig. 1, curve 3. Curve 4 was obtained by deriving  $A$  and  $B$  from the experimental points at 290° and substituting them into [3], as were curves 1 and 2 for the points at 260 and 300°C. Fig. 1 also shows calculated values at 310°C, curve 5. The curves at 260, 290, 300 and 310°C are practically unaffected by the

value chosen for  $G(\text{C}_6\text{H}_6^*)$ , there being less than 1 % variation when  $G(\text{C}_6\text{H}_6^*)$  is changed from 1.5 to 8.5.

(ii) Eqn. [1] can be written as

$$G(\text{H}_2) = G^1(\text{C}_6\text{H}_6^*) / \{1 + ABx/(1 + Bx)\},$$

where  $G^1(\text{C}_6\text{H}_6^*) = G(\text{C}_6\text{H}_6^*)/(1 + D + Cx)$  is the  $G$  value of those excited molecules which decompose. A consideration of the polymer production suggests that if this mechanism applies  $G^1(\text{C}_6\text{H}_6^*)$  is approximately half  $G(\rightarrow\text{polymer})$ . If we assume that the variation of  $G(\text{H}_2)$  with density is due to the term  $[(1 + ABx)/(1 + Bx)]$  in [1] and [2], i.e., that  $Cx \ll (1 + D)$ , then a variation of  $G^1(\text{C}_6\text{H}_6^*)$  with temperature could

TABLE 2  
ANALYSIS OF  $G(\text{H}_2)$  RESULTS

METHOD (i)								
$G(\text{C}_6\text{H}_6^*)$	$A_0$	$E_A$ kJ mole <sup>-1</sup>	$B_0$ ml g <sup>-1</sup>	$E_B$ kJ mole <sup>-1</sup>	$G(\text{H}_2)$ 350°	$G(\text{H}_2)$ 390°		
1.5	$3.85 \times 10^{-8}$	-87.6	0.120	27.2	0.902	1.23		
4.0	$5.42 \times 10^{-7}$	-80.5	1.61	-15.9	1.14	2.04		
8.5	$1.85 \times 10^{-6}$	-78.4	3.17	-13.0	1.24	2.57		
METHOD (ii)								
$G(\text{C}_6\text{H}_6^*)$	$D_0$	$E_D$ kJ mole <sup>-1</sup>	$A_0$	$E_A$ kJ mole <sup>-1</sup>	$B_0$ ml g <sup>-1</sup>	$E_B$ kJ mole <sup>-1</sup>	$G(\text{H}_2)$ 350°	$G(\text{H}_2)$ 390°
3.0	$5.62 \times 10^{-3}$	-25.7	$8.21 \times 10^{-7}$	-72.6	0.105	-27.5	0.960	1.46
6.0	$6.03 \times 10^{-2}$	-19.3	$8.21 \times 10^{-7}$	-72.6	0.105	-27.5	0.986	1.55
9.0	0.135	-17.8	$8.21 \times 10^{-7}$	-72.6	0.105	-27.5	0.993	1.57
12.0	0.216	-17.2	$8.21 \times 10^{-7}$	-72.6	0.105	-27.5	0.996	1.58
METHOD (iii)								
$G_0^1$	$E_G$ kJ mole <sup>-1</sup>	$S_0$ or $C_0$ ml g <sup>-1</sup>	$E_s$ or $E_c$ kJ mole <sup>-1</sup>	$G(\text{H}_2)$ 350°	$G(\text{H}_2)$ 390°			
$7.38 \times 10^6$	79.2	14.4	12.2	1.40	3.41			
METHOD (iv)								
$G(\text{C}_6\text{H}_6^*)$	$P_0$	$E_p$ kJ mole <sup>-1</sup>	$C_0$ ml g <sup>-1</sup>	$E_e$ kJ mole <sup>-1</sup>	$G(\text{H}_2)$ 350°	$G(\text{H}_2)$ 390°		
2.0	$1.70 \times 10^{-8}$	-91.4	14.4	12.2	0.937	1.26		
2.5	$3.98 \times 10^{-8}$	-88.5	14.4	12.2	1.01	1.45		
3.0	$7.09 \times 10^{-8}$	-86.7	14.4	12.2	1.06	1.61		
3.5	$1.09 \times 10^{-7}$	-85.5	14.4	12.2	1.10	1.74		

Values of  $G(\text{H}_2)$  at 350 and 390° are for a density of 0.163 g ml<sup>-1</sup>

be caused by the dependence of  $D = k_{2a}/k_1$  on temperature. Values of  $D$  were calculated at 260 and 300°C based on  $G^1(\text{C}_6\text{H}_6^*) = 0.5 G(\rightarrow\text{polymer})$  and were expressed as  $D_0 \exp(-E_D/RT)$  to give  $D_0$  and  $E_D$ ;  $G^1(\text{C}_6\text{H}_6^*) = G(\text{C}_6\text{H}_6^*)/(1 + D)$  could then be calculated at any temperature for a chosen value of  $G(\text{C}_6\text{H}_6^*)$ . Table 2 shows values  $D_0$  and  $E_D$  and of the parameters used in method (i), based on these assumptions, for various values of  $G(\text{C}_6\text{H}_6^*)$ . The calculated curve for  $G(\text{H}_2)$  against density at 290°C is within 1 % of that obtained from the constants of method (i). These considerations tend to show that the activation energy for hydrogen atom abstraction from benzene is considerably larger (40-80 kJ/mole) than for addition, and

that the activation energy for reaction (6) is about 24 kJ/mole below that for the decomposition of the cyclohexadienyl radical, which is 130 kJ/mole.<sup>25</sup> The defect of this mechanism is the very small value calculated for  $A_0$ , implying that the pre-exponential factor for reaction (3) is many powers of ten greater than that for (4), which is unlikely, since  $k_4$  at room temperature is already very large, ( $\sim 0.37 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  at 25°C).<sup>26</sup> Since  $G(\text{H}_2)$  increases by a large factor ( $\sim 10$ ), between 250 and 350°C, while  $G(\rightarrow \text{polymer})$  does not, an alternative possibility is that  $k_4$  is always much greater than  $k_3$ , but that the cyclohexadienyl radical formed in (4) can decompose in another way, viz.,



When this reaction is included, a steady-state treatment gives

$$G(\text{H}_2) = \frac{G(\text{C}_6\text{H}_6^*)}{\left\{1 + \frac{k_{2a}}{k_1} + \frac{k_2}{k_1}[\text{C}_6\text{H}_6]\right\}} \times \left\{ \frac{k_3}{k_3 + \frac{k_4(k_{5a} + k_6[\text{C}_6\text{H}_6])}{(k_4 + k_{5a} + k_6[\text{C}_6\text{H}_6])}} + \frac{k_{5a}}{(k_3 + k_4)(k_5 + k_{5a} + k_6[\text{C}_6\text{H}_6])k_5} \right\}$$

If the hydrogen arises predominantly from reaction (5a) rather than (3) the expression becomes

$$G(\text{H}_2) = G(\text{C}_6\text{H}_6^*) \left/ \left[ (1 + D + Cx) \frac{(A+1)}{A} \left\{ \frac{R}{(1+A)} + 1 + Sx \right\} \right] \right.$$

where  $R = k_5/k_{5a}$ ,  $S = k_6/k_{5a}$ . The graphs of  $1/G(\text{H}_2)$  against  $x$  are such that the slopes are not very dependent on temperature but the intercepts are, and this was interpreted in two ways.

(iii) We put  $G(\text{C}_6\text{H}_6^*)/(1 + D + Cx) = G^1$  and assume that  $Cx \ll D$ ,  $A \gg 1$ , and  $R/(1+A) \ll 1$ ; then

$$G(\text{H}_2) = G^1/(1 + Sx). \quad [4]$$

$S$  was expressed as  $S_0 \exp(-E_s/RT)$ , and  $G^1$  as  $G_0^1 \exp(-E_G/RT)$  and  $S_0$ ,  $E_s$ ,  $G_0$ ,  $E_G$  were obtained from the results at 260 and 300°. Results at 290, 310, 350 and 390°C were calculated as before, and are shown in table 2 and fig. 9. In this interpretation the variation with density is due to the competition between (6) and (5a), and the variation with temperature is due to the competition between (2a) and (1). A kinetically equivalent interpretation is that  $D \ll 1$ ,  $S \ll R/(1+A)$  and that  $G^1 = G(\text{C}_6\text{H}_6^*) \left/ \left[ \frac{(A+1)}{A} \frac{R}{(1+A)} + 1 \right] \right.$  and thus  $G(\text{H}_2) = G^1/(1 + Cx)$  so that the effect of density is due to the competition between the deactivation and decomposition of  $\text{C}_6\text{H}_6^*$ , and the dependence on temperature is due to its effect on the competition between (5) and (5a), i.e., the differing modes of decomposition of the cyclohexadienyl radical.

(iv) A way of taking account of polymer yields when reaction (5a) is introduced is to say that  $G^1(\text{C}_6\text{H}_6^*)$ , i.e., the yield at zero density of those excited benzene molecules which decompose, is about 2.5 to 3 at 260°C. The variation with density of both polymer and hydrogen is then accounted for by the competition between deactivation and decomposition of  $(\text{C}_6\text{H}_6^*)$ , if we assume that  $D = 0$ , and that the important reactions of  $\text{C}_6\text{H}_7\cdot$  are (5) and (5a), i.e., that  $S \approx 0$ . The expression for  $G(\text{H}_2)$  then becomes, with  $A \gg 1$ ,

$$G(\text{H}_2) = G(\text{C}_6\text{H}_6^*)/(1 + Cx)(P + 1) \quad [5]$$

where  $P = R/A$ . The slight variation of  $G(\rightarrow \text{polymer})$  with temperature is accounted for if at lower temperatures the predominant reaction of  $\text{C}_6\text{H}_7\cdot$  is its decomposition to  $\text{H}\cdot$  and  $\text{C}_6\text{H}_6$  so that it rarely contributes to polymer formation; in this case,  $G(\rightarrow \text{polymer}) \approx G(\text{C}_6\text{H}_6^*)$ , the polymer arising from  $\text{C}_6\text{H}_5\cdot$  radicals formed in reaction (2). As the temperature is raised the decomposition of  $\text{C}_6\text{H}_7\cdot$  to  $\text{H}_2$  and  $\text{C}_6\text{H}_5\cdot$  becomes increasingly important so that  $G(\rightarrow \text{polymer})$  approaches  $2 G(\text{C}_6\text{H}_6^*)$  since two  $\text{C}_6\text{H}_5\cdot$  radicals are formed for each  $\text{C}_6\text{H}_6^*$  decomposed. An analysis of the effect of temperature on eqn. [5] is given in table 2 and fig. 9.

All these methods yield reasonable agreement between theory and experiment up to  $350^\circ\text{C}$  but when competition, with consequent saturation of temperature effects, is included, the experimental  $G(\text{H}_2)$  at  $390^\circ\text{C}$  is higher than predicted. It is possible that between 350 and  $390^\circ\text{C}$  chain reactions begin to be important, and that  $\text{C}_6\text{H}_7\cdot$  also decomposes to smaller fragments, including  $\text{H}_2$ ; experimentally the yields of  $\text{C}_3$  and  $\text{C}_4$  hydrocarbons, which are very small up to  $310^\circ$ , increase markedly at 350 and  $390^\circ\text{C}$ .

### OTHER CONSIDERATIONS

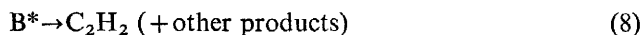
A feature of the results at  $260^\circ\text{C}$  is that  $G(\text{H}_2)$  is practically independent of density above  $0.103 \text{ g ml}^{-1}$ . This is certainly true from  $0.180$ – $0.400 \text{ g ml}^{-1}$ , at which values the fractions of the total mass in the liquid phase are  $0.533$  and  $0.924$  respectively. A parallel phenomenon was found in the effect of density in the radiolysis of propene,<sup>2</sup> and hence the similarity in the shape of the curves of  $G(\text{H}_2)$  against density in the two-phase and supercritical regions led the author to suggest that under irradiation a two-phase condition might persist into the supercritical region. Our results show a greater sensitivity of  $G(\text{H}_2)$  to changes in density at  $290$  and  $300^\circ\text{C}$  than at  $260^\circ\text{C}$  and hence this is unlikely to occur with benzene.

Other possible explanations for the large effect of temperature on  $G(\text{H}_2)$  are the production of hydrogen in the aromatization of unsaturated molecules such as cyclohexadienes and phenyl cyclohexadienes, and the formation of hydrogen in a chain reaction. For the former possibility, the individual yield of such molecules is small, although the total effect might possibly be enough to produce large changes in  $G(\text{H}_2)$ . Chain reactions have been postulated to explain temperature effects and changes in the nature of condensed products in the radiolysis of aliphatic<sup>27</sup> hydrocarbons at temperatures near those at which thermal cracking occurs, and to explain such effects and dose-rate effects in the radiolysis of aromatic<sup>9, 28</sup> hydrocarbons. However, in the latter cases the large changes with temperature requiring such a postulate were predominately in  $G(\rightarrow \text{polymer})$ , and our measurements up to  $350^\circ\text{C}$ , show no similar great increase in  $G(\rightarrow \text{polymer})$  from  $260$  to  $350^\circ\text{C}$ , although  $G(\text{H}_2)$  increases tenfold in this range. It is difficult to devise a chain mechanism which gives large increases in  $G(\text{H}_2)$  but not in  $G(\rightarrow \text{polymer})$ .

Although table 1 shows that  $G(\text{H}_2)$  does not change markedly with dose up to  $\sim 4.6 \times 10^{20} \text{ eV g}^{-1}$ , fig. 4 shows that at increasing dose  $G(\text{H}_2)$  decreased to less than  $0.05$ , i.e., less than  $\frac{1}{6}$  of the low-dose value. This effect was not observed in the hydrogen yield from biphenyl, or from ortho-, meta-, or paraterphenyl irradiated with  $\gamma$ -rays or pile radiation,<sup>29-31</sup> and is probably due to thermal hydrogenation of the more reactive small molecules formed in greater yield in the radiolysis of benzene than when the larger aromatic molecules are irradiated. For instance, acetylene is formed in greater yield from benzene, and results on its homogeneous hydrogenation<sup>32</sup> at  $495$  to  $535^\circ\text{C}$ , when extrapolated to our temperatures, suggest that, although at low doses this reaction is negligible, this is not so for the longer irradiations.

## ACETYLENE YIELDS

The low-dose acetylene yields of fig. 2 show that below 300°C, as in the liquid phase,<sup>17</sup>  $G(\text{C}_2\text{H}_2)$  is of comparable magnitude to  $G(\text{H}_2)$ . But in contrast with the results of fig. 1,  $G(\text{C}_2\text{H}_2)$  is more dependent on density than  $G(\text{H}_2)$ , the decrease in the region 0.04–0.3 g ml<sup>-1</sup> being greater than that in  $G(\text{H}_2)$ ; also  $G(\text{C}_2\text{H}_2)$  does not increase with temperature, the decrease in the range 300–350°C possibly being due to its thermal reactions such as polymerization.<sup>32</sup> It is possible that acetylene arises from the decomposition of electronically-excited molecules which can also be deactivated by collision:<sup>5</sup>



The mechanism consisting of (7), (8) and (9) should give a linear plot for  $1/G(\text{C}_2\text{H}_2)$  against density and a least-squares calculation gives  $k_8/k_9 = 0.048 \text{ g ml}^{-1}$ ,  $G(\text{B}^*) = 0.605$ . The resultant calculated curve of  $G(\text{C}_2\text{H}_2)$  against density is shown in fig. 2.

Fig. 5 shows that at higher doses and longer times  $G(\text{C}_2\text{H}_2)$  decreases rapidly and at the highest doses was not measurable. This is probably due to its simultaneous thermal hydrogenation (which gives  $\text{C}_2\text{H}_4$  and eventually  $\text{C}_2\text{H}_6$ ) and polymerization, which occur rapidly at 490°C and above.<sup>32</sup> The decrease in  $G(\text{C}_2\text{H}_2)$  is greater than that in  $G(\text{H}_2)$  and is greater than the increase in  $G(\text{C}_2\text{H}_4)$  and  $G(\text{C}_2\text{H}_6)$ , suggesting that hydrogen is also reacting with substances other than acetylene, and that the main reaction removing acetylene is its own polymerization. A parallel reduction in acetylene yield with increasing dose was found at 300°C in the electron irradiation of biphenyl.<sup>33</sup>

## YIELDS OF ETHYLENE, ETHANE, AND METHANE

Methane, the yields of which are very small at low doses and increase with increasing dose, is probably produced, at least partly, by the secondary breakdown of the polymer product. Fig. 7, however, shows an effect of density greater than that in  $G(\rightarrow \text{polymer})$  suggesting that some, at least, must be formed in a density-dependent mechanism, such as from secondary reactions of acetylene, whose yield is more density-dependent. Ethylene and ethane (fig. 3) have density-dependent yields at low doses, and the yield/dose relationship (table 1) suggests that they are secondary products. Furthermore, the effect of temperature on the ethane yield (fig. 3) parallels that on  $G(\text{H}_2)$  (fig. 1), so that it appears likely that ethane is formed by reaction of hydrogen with acetylene even at low doses. At higher doses (fig. 5) it seems probable that secondary reactions are occurring, and that ethylene is first formed and at longer times is further hydrogenated to yield ethane. Fig. 7 shows effects of density at high dose (and time) which may therefore be due to the dependence on density of the primary hydrogen and acetylene yields. The ethylene yield at low dose is not very dependent on temperature, and the result at 350° is lower than those at 290 and 300°C; this may be due to the effect of temperature on its hydrogenation to ethane.

## YIELDS OF POLYMER AND BIPHENYL

Although  $G(\rightarrow \text{polymer})$  appears to decrease slightly with dose, as do the corresponding yields for irradiated biphenyl<sup>29</sup> and terphenyls,<sup>29, 30</sup> fig. 6 shows that the variation with dose of  $G(\rightarrow \text{polymer})$  and  $G(\text{biphenyl})$  in the dose range employed is small. This can be reconciled with the dependence on dose of the other products (fig. 5) on the grounds that the latter generally have  $G$  values much lower than



$G(\rightarrow \text{polymer})$  and that changes in the polymer composition must be occurring with dose and time. Even at  $350^\circ\text{C}$  the polymer yield is low compared with the  $G$  value for conversion to other products for aliphatic and alicyclic hydrocarbons at room temperature, (e.g.,  $G(-\text{C}_6\text{H}_{12})$  for cyclohexane is  $\sim 7$ ).<sup>34</sup> The small variation of  $G(\rightarrow \text{polymer})$  with density could be due to the deactivation of excited molecules which decompose as in (1) eventually to give polymer. In the mechanism given in reactions (1)-(9), polymer will be formed in the early stages by combination and disproportionation of the radicals ultimately formed, and in the later stages by reaction of these radicals with product molecules.

Every H atom formed in (1) reacts to give another radical; if we assume that the phenyl radical at these temperatures predominantly abstracts, then if the  $\text{C}_6\text{H}_7\cdot$  radical adds to surrounding molecules  $G(\rightarrow \text{polymer})$  will be between 2 and 3 times the  $G$  value of decomposing excited molecules,  $G^1(\text{C}_6\text{H}_6^*)$ . However, if the predominant reaction of  $\text{C}_6\text{H}_7\cdot$  is decomposition,  $G(\rightarrow \text{polymer})$  will be between  $G^1(\text{C}_6\text{H}_6^*)$  and  $2G^1(\text{C}_6\text{H}_6^*)$  depending on whether the decomposition is to  $\text{C}_6\text{H}_6 + \text{H}\cdot$ , or to  $\text{C}_6\text{H}_5\cdot + \text{H}_2$ . According to the mechanisms given above the effect of increased temperature will be to increase the yield of phenyl radicals, and this is borne out by the increasing yield of biphenyl with increasing temperature (fig. 2 and table 1).

#### GENERAL CONCLUSIONS

The main features of the results are consistent with the formation of products by the reaction of radicals formed when electronically excited molecules decompose. A suggestion based on room-temperature results for the liquid, viz., that decomposition occurs when excited molecules interact in spurs or tracks,<sup>5</sup> cannot be supported at high temperatures ( $> 260^\circ\text{C}$ ) since the diffusion out of spurs is very fast. It appears that the intermediates formed at high temperatures are more easily subject to dissociation than those formed at room temperature. The large effect of temperature on  $G(\text{H}_2)$  can be interpreted in terms of competitive reactions of H atoms or radicals, without recourse to a chain reaction mechanism, so that the concept that hydrogen is produced in zones of high temperature<sup>7, 9</sup> in which ambient temperature effects are small, does not appear to apply to our system.

The effect of temperature on gamma-ray yields is pertinent to the thermal spike model of L.E.T. effects, in which it is suggested that the effect of increasing L.E.T. is due to the thermal decomposition of the same products or intermediates as are formed by gamma-radiation. Although in general product yields, e.g., of hydrogen and conversion to polymer, increase with temperature as they do with increasing L.E.T., the increases for individual products are not related to each other in the same way. For instance, hydrogen yields increase with temperature and at  $350^\circ$  are about 50 times bigger than the acetylene yields; the latter are invariant or decrease with increasing temperature from  $290^\circ$  to  $350^\circ\text{C}$ . However, with increasing L.E.T. at room temperature the acetylene yield remains at about half the hydrogen yield up to about  $200\text{ eV/nm}$ <sup>6</sup> and even with fission fragments the yields are approximately equal.<sup>35</sup>

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