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THE RADIOLYSIS OF THE XYLENE ISOMERS AND ETHYLBENZENE

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ABSTRACT

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The G-values for the formation of H_2 and CH_4 in the ^{60}Co γ -radiolysis of the xylene isomers and ethylbenzene have been compared. The presence of iodine does not affect G_{H_2} , but reduces G_{CH_4} to a limiting value. For p-xylene G_{H_2} and the unscavengeable CH_4 yield are independent of temperature from 20° to $110^\circ C$, whereas the total CH_4 yield increases six-fold over this range. The H_2 and CH_4 yields are greatly reduced in the solid state, and in the liquid state benzene shows a protective effect on the yields of both gases. The formation of CH_4 and C_2 - hydrocarbons was compared with the C_6 - and C_7 - products for p-xylene and ethylbenzene, and isomerisation has been shown to occur to a negligible extent. The production of high molecular weight products was measured for the xylenes, and is independent of dose rate and temperature for liquid p-xylene, but is decreased in the solid state. The results are qualitatively consistent with the reactions of radicals and excited molecules.

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The radiation chemistry of toluene has been studied in detail⁽¹⁻⁵⁾, but

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- (1) J. P. Manion and M. Burton, J. Phys. Chem., 56, 560 (1952).
 - (2) R. R. Hentz and M. Burton, J. Am. Chem. Soc., 73, 532 (1951).
 - (3) T. J. Sworski and M. Burton, J. Am. Chem. Soc., 73, 3790 (1951).
 - (4) R. B. Ingalls, J. Phys. Chem., 65, 1605 (1961).
 - (5) J. Hoigne' and T. Gäumann, Helv. Chim. Acta, 44, 2141 (1961).
-

other alkyl benzenes have received comparatively little attention. The yields of the gaseous products from the radiolysis of toluene, mesitylene and ethylbenzene⁽²⁾, and of i-propylbenzene and t-butylbenzene⁽⁶⁾ have indicated the in-

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- (6) T. J. Sworski, R. R. Hertz and M. Burton, J. Am. Chem. Soc., 73, 1998 (1951).
-

fluence of the number and complexity of alkyl groups in the molecule. In addition it has been demonstrated that the gas yields of alkyl benzenes vary with the type of radiation^(3,7). The spectrum of products of lower molecular weight

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- (7) M. A. Sweeney, Univ. of California Radiation Laboratory Report, UCRL-9983, March, 1962.
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has been established for i-propylbenzene^(7,8).

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- (8) R. R. Hentz, J. Phys. Chem., 65, 1470 (1961).
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To extend the study of the effect of structure to that of the ring position of substituents on the radiation chemistry of simple alkyl-aromatic hydrocarbons the ⁶⁰Co γ-radiolysis of the xylene isomers and ethylbenzene has been investigated. Since the influence of temperature has generally been neglected, the

radiolysis of p-xylene has been examined over a wide temperature range.

EXPERIMENTAL

Materials

All hydrocarbons were Phillips Research Grade. They were further purified by repeated shaking with concentrated H_2SO_4 until the acid layer was colourless, and then washing with 10% Na_2CO_3 solution and several times with distilled water. After drying with anhydrous CaSO_4 and filtering, the hydrocarbons were distilled under vacuum in a greaseless system, the middle 80% fraction being collected and stored in evacuated vessels until used.

Iodine was Fisher Scientific Company, certified reagent (resublimed). Oxygen was General Dynamics Corporation 99.5% pure. Tetrachloroethylene (Eastman Organic Chemicals, spectro grade) was dried with anhydrous CaSO_4 , filtered and distilled under vacuum, the middle fraction of 50% being collected and used immediately.

Irradiation Technique

The previously degassed hydrocarbons were distilled under vacuum into a calibrated tube and after volume determination distilled into the irradiation vessels fitted with break-seals. Mixtures, and solutions of I_2 or C_2Cl_4 were prepared with hydrocarbons which had been twice distilled under vacuum, and were pipetted into the vessels, degassed and sealed off under vacuum. Samples containing O_2 were sealed off at measured pressures of O_2 . The volumes of liquid used were from 5 to 15 ml.

An under-water ^{60}Co γ -facility was employed and the samples were irradiated in air at the ambient temperature of the source ($20 \pm 1^\circ \text{C}$), in an

oil bath controlled to $\pm 1^\circ \text{C}$ or in Dewar vessels containing cooling liquids. The rates of energy absorption in the hydrocarbons were calculated on the basis of electron densities from dose rates measured with the ferrous sulphate dosimeter assuming $G_{\text{Fe}^{3+}} = 15.5^{(9)}$.

(9) R. H. Schuler and A. O. Allen, J. Chem. Phys., 24, 56 (1956).

Analysis

After irradiation the sample tubes were sealed on to a modified Saunders-Taylor apparatus⁽¹⁰⁾ and the total quantity of gas which could be obtained by

(10) K. W. Saunders and H. A. Taylor, J. Chem. Phys., 9, 616 (1941).

repeated freezing, expansion and melting cycles was measured. Degassing at -196°C did not remove all the CH_4 from the samples, but the gas collected by degassing at -119°C ($\text{C}_2\text{H}_5\text{Br}$ slush) contained all the H_2 and CH_4 produced. When C_2H_4 solutions were irradiated the -119°C fraction contained HCl which was removed by a plug of crushed KOH pellets located between the sample and the measuring apparatus. The C_2 - hydrocarbons were completely removed by degassing at -23°C (CCl_4 slush). The collected gases were transferred in calibrated tubes for gas chromatographic analysis.

Analyses were performed with a Perkin-Elmer model 154 Vapor Fractometer, using a thermistor detector, 1 mV recorder, helium carrier gas and columns supplied by Perkin-Elmer. H_2 and CH_4 (and O_2) were determined on a 2-metre actuated charcoal column at 45°C and their identities and ratio of yields confirmed by mass spectrometry. For samples collected at -23°C the ratio of each of the C_2 gases

to CH_4 was determined on a 2-metre silica gel column at 45°C . Analyses on this column of samples collected at -119° indicated less than 1% of C_2 hydrocarbons in this fraction. The identities of the C_2 -hydrocarbons were confirmed by their retention times on a 2-metre modified (di-2-ethylhexyl sebacate added) silica gel column at 52°C .

To study the higher molecular weight products ampoules were filled and irradiated just prior to analysis to minimize any post-irradiation effects. Samples of the irradiated liquid were analysed on a 4-metre 7,8-benzoquinoline column at 95°C . This column resolves benzene, toluene, the three xylene isomers and ethylbenzene, but does not separate m-xylene, p-xylene and ethylbenzene when one of these is present in large excess.

The total irradiation products which are less volatile than the parent xylenes ie "polymer" were isolated by vacuum distillation of the irradiated liquids, kept at 20°C , until a piece of solid CO_2 pressed against the neck of the tube from which the hydrocarbon was being distilled caused no condensation of liquid at that point. In all cases this gave viscous yellow liquids which by chromatographic analysis were shown to always contain less than 7.5% of the parent hydrocarbon. After weighing, the average molecular weights of the residues were measured in toluene solution using a Mechrolab Inc., Vapor Pressure Osmometer model 301 calibrated with biphenyl and p-terphenyl.

RESULTS

Formation of Gaseous Products

The yields of H_2 and CH_4 obtained on the radiolysis of the pure liquid hydrocarbons at 20°C were in all cases proportional to the absorbed dose over

the range 1×10^{20} to 2×10^{21} eV gm⁻¹ at a dose rate of 4×10^{15} eV gm⁻¹sec⁻¹. Figure 1 shows the results for o-xylene and the yields from the hydrocarbons studied are summarized in Table 1, which also shows the yields of H₂ and CH₄ from the hydrocarbons containing iodine at concentrations in the range 3×10^{-3} to 5×10^{-2} M, the G-values being independent of the I₂ concentration. G_{H2} increases slightly on adding I₂ to the hydrocarbons, whereas for benzene Schuler⁽¹¹⁾

 (11) R. H. Schuler, J. Phys. Chem., 60, 381 (1956).

obtained a slight decrease at comparable I₂ concentrations. The ratio G_{CH4}/G_{H2} (0.164) for ethylbenzene agrees closely with the data of Hentz and Burton⁽²⁾ for 1.8 MeV electrons, but the individual G-values are about 10% lower than obtained by these authors.

In the case of p-xylene ampoules were sealed off containing approximately measured pressures of oxygen. After irradiation at 20° C and a dose rate of 3.97×10^{15} eV.gm⁻¹sec⁻¹ the H₂, CH₄ and excess O₂ were collected and analysed. For O₂ pressures exceeding 50 mm the yields were G_{H2} = 0.217 and G_{CH4} = 0.0029. At lower O₂ pressures G_{H2} was unchanged but G_{CH4} increased progressively to its value for the pure hydrocarbon, indicating competition between O₂ and p-xylene for the methyl radicals. Irradiation under the same conditions of p-xylene containing tetrachloroethylene, at concentrations from 0.014 M to 0.15 M caused no change in the values of G_{H2} or G_{CH4}. C₂Cl₄ is known to scavenge H atoms produced in the radiolysis of hexane⁽¹²⁾, but it apparently does not scavenge methyl

 (12) T. J. Hardwick, J. Phys. Chem., 64, 1623 (1960).

radicals, at least, those produced in the radiolysis of p-xylene.

Table I. 100 eV yields from ^{60}Co γ -radiolysis of hydrocarbons at $20^\circ \pm 1^\circ \text{C}$

Hydrocarbon	Dose Rate $\text{eV} \cdot \text{gm}^{-1} \text{sec}^{-1} \times 10^{-15}$	Pure Hydrocarbon		Hydrocarbon + I_2	
		G_{H_2}	G_{CH_4}	G_{H_2}	G_{CH_4}
Ethylbenzene	3.73	0.158	0.0259	0.163	0.0058
o-Xylene	3.97	0.235	0.0171	0.246	0.0028
m-Xylene	3.73	0.184	0.0142	0.197	0.0028
p-Xylene	3.97	0.209	0.0144	0.219	0.0030
	0.852	0.203	0.0145	-	-
	72.7	0.200	0.0138	-	-
	128	0.216	0.0147	-	-

For p-xylene the yields of H_2 and CH_4 were measured over a range of dose rates and the results, included in Table I, show the formation of both products is independent of dose rate from 8.5×10^{14} to 1.3×10^{16} $eV\ gm^{-1}sec^{-1}$. The effect of temperature on the gas yields from liquid and solid p-xylene is shown in Table II. The production of H_2 and CH_4 was linear with absorbed dose except for the CH_4 yields at 82° and 110° C which decreased slightly at doses exceeding 8×10^{20} $eV\ gm^{-1}$ so that the G-values were calculated from the initial slopes of the yield curves. In the liquid phase the yields were also measured in the presence of iodine at concentrations from 5×10^{-3} to 5×10^{-2} M. The gases formed in solid p-xylene (m.p. 13° C) were isolated by melting and then degassing by the usual procedure.

The radiolysis of p-xylene and ethylbenzene produced ethane, ethylene and acetylene with the yields given in Table III. The G-values were independent of dose in the range 6 to 30×10^{20} $eV\ gm^{-1}$. No propane was detected in p-xylene samples irradiated to the higher doses.

Formation of C_6 and Higher Products

For p-xylene irradiated at 20° C at a dose rate of 7.02×10^{16} $eV\ gm^{-1}sec^{-1}$ to doses in the range 5 to 14×10^{21} $eV\ gm^{-1}$, toluene was produced with a G-value of 0.014. No benzene or o-xylene was detected and analysis of test mixtures indicated that if they are formed they must have G-values less than 0.002. The products of o-xylene irradiated under the same conditions contained no benzene, ethylbenzene or p-xylene, but did contain toluene ($G = 0.023$) and m-xylene ($G = 0.042$). Similarly radiolysis of ethylbenzene produced benzene ($G = 0.016$) and toluene ($G = 0.018$) but no detectable o-xylene. For m-xylene irradiated to lower total doses no benzene, toluene or o-xylene were detected, indicating their

Table II. G-values for p-xylene irradiated at dose rate of $3.73 \times 10^{15} \text{ eV} \cdot \text{gm}^{-1} \cdot \text{sec}^{-1}$

Temperature °C	Pure p-xylene		p-xylene $\rightleftharpoons$ iodine	
	G_{H_2}	G_{CH_4}	G_{H_2}	G_{CH_4}
-196	0.0112	6.4×10^{-4}	-	-
- 80	0.0196	7.3×10^{-4}	-	-
0	0.0493	10.5×10^{-4}	-	-
20 ^a	0.209	0.0144	0.219	0.0030
49.5	0.194	0.0154	0.203	0.0026
82	0.200	0.0224	0.201	0.0024
110	0.199	0.0867	0.208	0.0024

^a Dose rate $3.97 \times 10^{15} \text{ eV} \cdot \text{gm}^{-1} \cdot \text{sec}^{-1}$.

Table III. G-values for the formation of C₂-products at 20° C.

Hydrocarbon	Dose Rate eV.gm ⁻¹ sec ⁻¹ x10 ⁻¹⁵	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
p-Xylène	3.44	0.0033	0.0002	0.0001
Ethylbenzene	3.52	0.0021	0.0071	0.0057

G-values to be less than 0.05. In none of the irradiated samples did the chromatograms show any unidentified peaks which eluted before o-xylene, so that the liquid products are predominantly of higher molecular weight than the parent compounds.

The yields and average molecular weights of the "polymer" produced from the xylene isomers irradiated under various conditions are summarized in Table IV. The G-values calculated as loss of the irradiated hydrocarbon are independent of dose over the ranges studied, and the molecular weights increase continuously, but not linearly, with dose. Radiolysis of p-Xylene-Benzene mixtures.

To determine whether the radiolysis of p-xylene could be influenced by the presence of a second aromatic molecule the formation of H_2 and CH_4 was measured in the radiolysis of mixtures of p-xylene and benzene over the full range of compositions. From Figure 2, in which each point is the average of three measurements, it is seen that the values of G_{H_2} and G_{CH_4} based on total energy absorbed in such mixtures are both less than predicted (dotted lines) simply on the basis of electron fraction.

DISCUSSION

The yields of H_2 from ethylbenzene and the xylenes are effectively unchanged by radical scavengers so that none of the H_2 results from H atoms which have escaped from the solvent cage of their parent molecules. Similar conclusions were made by Schuler⁽¹¹⁾ in the case of benzene, and are consistent with the high rate constants for addition of H atoms to these hydrocarbons⁽¹³⁾.

(13) T. J. Hardwick, J. Phys. Chem., 66, 117 (1962).

Table IV. G-values and average molecular weights of the "polymer" produced on radiolysis of the isomeric xylenes.

Hydrocarbon	Temp., °C	Dose Rate $\text{eV} \cdot \text{gm}^{-1} \text{sec}^{-1} \times 10^{-16}$	Dose Range $\text{eV} \cdot \text{gm}^{-1}$	G(-Hydrocarbon)	Range of Mol. Wts.
o-Xylene	20	6.86	9.88×10^{20} to 1.18×10^{22}	1.34	253 to 289
m-Xylene	20	7.01	1.26×10^{21} to 1.97×10^{22}	0.99	272 to 308
p-Xylene	20	7.02	6.06×10^{21} to 1.40×10^{22}	1.10	282 to 299 ^a .
p-Xylene	20	0.344	5.94×10^{20} to 3.00×10^{21}	1.07	260 to 269
p-Xylene	110	0.344	8.15×10^{20} to 2.09×10^{21}	1.17	267 ^b .
p-Xylene	-80	0.344	1.42×10^{21} to 3.66×10^{21}	0.43	230 ^c .

a. Repeat sample irradiated to dose of $1.4 \times 10^{22} \text{ eV} \cdot \text{gm}^{-1}$ and in which residue was kept at 50° C and evacuated for 72 hours gave residue of molecular weight 345 instead of 299.

b. Dose = $1.89 \times 10^{21} \text{ eV} \cdot \text{gm}^{-1}$

c. Dose = $3.66 \times 10^{21} \text{ eV} \cdot \text{gm}^{-1}$

If initially formed H atoms were to abstract a second H atom from an adjacent xylene molecule then the actuation energy of this reaction⁽¹⁴⁾ would cause

 (14) R. B. Ingalls and J. R. Hardy, Can. J. Chem., 38, 1734 (1960).

G_{H2} to be temperature dependent, whereas for p-xylene the activation energy for G_{H2} is 0.0 ± 0.3 Kcal.mde⁻¹. On passing from liquid to solid p-xylene G_{H2} decreases sharply to a value which varies slightly with temperature. A mechanism of the type discussed by Burr^(15, 16) and Burns⁽¹⁷⁾ can account for these results.

 (15) J. G. Burr and J. M. Scarborough, J. Phys. Chem., 64, 1367 (1960).

(16) J. G. Burr, Nucleonics, 19, No. 10, 49 (1961).

(17) W. G. Burns, Trans. Faraday Soc., 58, 961 (1962).

In the liquid phase a small proportion of the H₂ results from a temperature independent unimolecular dissociation of an excited molecule,

the possibility of the reaction occurring in two stages being included in equation (1) in which the brackets enclose species which have not been separated by diffusion from the solvent cage in which they were formed.

The majority of the H₂ is produced by bimolecular reactions of the excited molecules

reaction (4) being included to explain LET effects⁽¹⁷⁾. In the solid state H_2 arises predominantly by reaction (1), whereas increased diffusion in the liquid phase favours reactions (2) (3) and (4) which must each have zero activation energy to account for the temperature independence of G_{H_2} . Moreover it is necessary to assume that the excited molecules do not react with radical scavengers.

According to Ingalls⁽⁴⁾ the hydrogen from toluene radiolysis is derived mainly from the methyl group, but some can arise from the aromatic ring by a H atom adding to toluene and the adduct disproportionating with a second H atom from another toluene molecule. Scavengers should react with this second H atom and also with the first H atom if it diffuses from the solvent cage in which it is formed, and reduce the H_2 yield so that a similar reaction apparently does not occur in the xylenes.

At 20° C the presence of I_2 or O_2 decreases the CH_4 yields to a limiting value about 20% of that in the absence of scavengers, so that the majority of the CH_4 is formed by abstraction reactions of freely diffusing methyl radicals formed in reaction (5). The yield of C_2H_6 from p-xylene shows combination $CH_3 \cdot C_6H_4 \cdot CH_3^* \longrightarrow CH_3 \cdot C_6H_4 \cdot + CH_3 \cdot$ of methyl radicals to be negligible. (5) The increase in G_{CH_4} with temperature may be due to the increased probability of escape of methyl radicals from the solvent cage in which they are formed, and to the higher activation energy for abstraction compared with addition reactions of these radicals. Since the yield of CH_4 in solid p-xylene is much less than the unscavengeable yield in the liquid phase, the latter which is independent of temperature must arise by two or more processes, which may be analogous to those for H_2 production.

There is evidence⁽¹⁸⁾ that in aromatic mixtures the unimolecular formation

(18) P. J. Dyne and J. Denhartog, Can. J. Chem., 40, 1616 (1962).

of hydrogen (ie both H atoms from the same molecule) is uninfluenced by the nature of the solvent, but that the bimolecular production of hydrogen does vary with the solvent. Toluene is the only other alkyl-benzene for which the radiolysis of its mixtures with benzene has been studied over the full concentration range⁽¹⁾. The H_2 and CH_4 (but not C_2H_2 and C_2H_4) formation obeyed the simple mixture law, so that its behavior differs from that of p-xylene. Since the ionization potentials of toluene and p-xylene are both less than that of benzene⁽¹⁹⁾

(19) G. F. Crable and G. L. Kearns, J. Phys. Chem., 66, 436 (1962).

it is unlikely that charge transfer is the cause of the protection. Preferential addition of H atoms and CH_3 radicals to one component of the mixture does not appear to be an explanation, at least for H_2 , since a small proportion of benzene produces a marked fall in G_{H_2} and the rate constant for addition of H atoms to p-xylene exceeds that for addition to benzene⁽¹³⁾. A greater probability for the occurrence of reaction (2) if the unexcited species is benzene could explain the observations in these mixtures, but the present work provides no direct evidence on this point.

The lack of influence of scavengers or temperature on the H_2 yield would be expected if it arose from the reactions of "hot" hydrogen atoms, whereas the CH_4 yield, which is affected by these variables, does not result from hot methyl radicals. The mechanisms for formation of H_2 and C_2H_2 in the radiolysis of benzene are apparently similar⁽¹⁷⁾, so that if hot H atoms were involved, it would be

necessary to assume their interaction with benzene could form acetylene, whereas there is evidence for the addition of recoil tritium atoms to the benzene ring⁽²⁰⁾.

(20) A. N. Nesmeyanov, et al., Radiokhimiya, 4, 116 (1961).

The very low yields of C_2 products from p-xylene indicate that ring fission is much less important than in the case of benzene where the acetylene yield is six-fold higher⁽¹⁾.

Comparable yields of CH_4 and toluene were obtained on radiolysis of either o-xylene or p-xylene at 20° C, so that the reaction⁽⁵⁾ followed by both radicals abstracting H atoms must be the principal source of toluene, and has been shown to account for 80% of the CH_4 . Similarly for ethylbenzene the sum of the C_2 hydrocarbon yields is of the same order of magnitude as the benzene yield. In the case of toluene $G_{Benzene}$ ⁽⁵⁾ is nearly twice the value of G_{CH_4} ⁽¹⁾ so that ethylbenzene and the xylenes should be formed with a total yield of approximately G_{CH_4} .

The very small or zero yields for isomerisation of the xylenes obtained in this work are contrary to a preliminary report by Gelbshtein et al⁽²¹⁾, who

(21) A. I. Gelbshtein, et al., All-Union Conference on Radiation Chemistry,

Moscow 1957. Abstracts of papers AEC-TR-2925, Part 4, p. 27. N.B. Full paper did not appear in the Proceedings of the Conference.

stated that under γ -irradiation at room temperature each of the three xylenes is isomerised into the other two, the G-values for the products being between 2 and 6.

The G-values for the conversion of xylene molecules to products of higher molecular weight are of the same order of magnitude as the corresponding values for benzene⁽²²⁾ and toluene⁽²⁾, and show the formation of

 (22) S. Gordon, A. R. Van Dyken and T. F. Doumani, J. Phys. Chem., 62,
 20 (1958).

"polymer" to be independent of dose rate and temperature in liquid p-xylene. The formation of polymer in p-xylene by pile irradiation has been observed⁽²³⁾

 (23) F. Van Hecke, Nature, 186, 382 (1960).

but no absolute yield was determined. The molecular weights of the products indicate a progressive increase in the average size of the polymer molecules with dose, and show that the average number of monomer units per polymer molecule is close to that for the case of benzene at similar doses⁽²⁴⁾. If all the H₂

 (24) W. N. Patrick and M. Burton, J. Am. Chem. Soc., 76, 2626 (1954).

from liquid p-xylene were formed by reactions (3) and (4), then G-(p-xylene) for the formation of polymer would be 2G_{H2} and the molecular weight would be 210. Therefore, other processes which are independent of temperature and dose rate must account for the majority of the polymer. These could involve excited molecules⁽¹⁷⁾ or be the subsequent addition reactions with each other, with xylene molecules or polymer molecules of the radicals resulting by reactions (6) and (7) from the dissociation of p-xylene in the solvent cage.

The molecular weight of the polymer formed in p-xylene irradiated in the solid state shows it to be mainly dimer. This probably results from the combination of the radicals formed in reactions (6) and (7), either at -80°C or as the solid is warmed up prior to analysis: the low yield of H_2 in the solid state signifies negligible contribution of reactions (3) and (4) to polymer formation in the solid.

The stability of the xylenes with regard to the formation of H_2 , CH_4 and high molecular weight products decreases on the order meta, para, ortho. No significance can be attached to a comparison of stabilities with ionisation potentials since these differ little between the xylenes⁽¹⁹⁾, however, the sequence of stabilities is the same as that of the C-H bond dissociation energies⁽²⁵⁾. The influence of the positions of ring substituents have been

(25) M. Szwanc, Chem. Revs., 47, 75 (1950).

examined for the terphenyls⁽²⁶⁾ and substituted toluenes⁽²⁷⁾ but the results

(26) E. L. Colichman and R. H. J. Gercke, Nucleonics, 14, No. 7, 50 (1956).

(27) R. M. Wagner and L. H. Towle. WADC Technical Report 58-683 (1959).

are not directly comparable with the present work.

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FIG. 1.

FIG. 2.

LEGENDS

Figure 1. The formation of H_2 and CH_4 in the ^{60}Co γ -radiolysis of o-xylene at $20^\circ C$. Dose rate = $3.97 \times 10^{15} \text{ eV gm}^{-1} \text{ sec}^{-1}$. Samples degassed at $-119^\circ C$ ($\odot$) and $-196^\circ C$ ($\bullet$)

Figure 2. The G-values for the formation of H_2 and CH_4 in the ^{60}Co γ -radiolysis of mixtures of benzene and p-xylene at $20^\circ C$. Dose rate = $7.27 \times 10^{16} \text{ eV gm}^{-1} \text{ sec}^{-1}$.