tions which affect the yield and determine the nature of the products.

$$RX \rightsquigarrow RX^+ + e$$
$$RX + e \longrightarrow R + X^-$$

The reaction of X^- with RX^+ may result in reactions in which hydrogen is split out or in which the carbon chain is split into two particles each containing a halogen. Current studies by Hamill and Williams in these laboratories using radiohalogens as tracers may furnish information on these reactions.

6.4. Impurity Reactions.—Two of the most common impurities with which we have to deal in kinetics are oxygen and water. Both, as it is shown in Table VII, are effective in capture of thermal electrons. Thus, when they are present as impurities (*e.g.*, in the system M), they are particularly likely to be troublesome because the principal neutralization will no longer be

$$M^+ + e \longrightarrow M^*$$

but will involve negative ions and may, when M is of sufficiently high ionization potential, not involve M^+ at all.

6.5. Water.—In liquid water the important primary reactions are

$$H_2O \rightsquigarrow H_2O^+ + e \qquad 6.5(1)$$
$$H_2O^+ + aq. \longrightarrow H_3O^+ + OH \qquad 6.5(2)$$

and

$$H_2O,\ aq. + e \longrightarrow H + OH^-,\ aq. \qquad 6.5(3)$$

The latter reaction is of special interest for this paper. As we see from Table VII, the isolated water molecule cannot capture an electron, for the H–OH bond strength most probably exceeds the electron affinity of the isolated OH^- ion. In water vapor at high pressure, just as in liquid water, solvation becomes important. The electron affinity of the solvated OH^- ion is very high. Reaction 6.5 (3) is very exothermic and the potential energy curves are perhaps to be represented by Fig. 4. The reaction corresponds to 6.1(2). Ultimately the H_3O^+ and OH^-,aq. ions produced some distance from each other diffuse together and combine. The average H^+ and OH^- concentration throughout the solution is not significantly affected by these phenomena (except insofar as H_2O_2 produced in the radiolysis may affect the *p*H) but as Professor James Franck has recently pointed out to us (private communication) local high concentrations of either H^+ or OH^- ions produced by irradiation of aqueous systems may have profound consequences in biological material. Living material is extremely sensitive to *p*H and may suffer serious changes before diffusion can moderate local acute ion concentrations.

NOTRE DAME, INDIANA RECEIVED JULY 20, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Studies in Photochemistry and Radiation Chemistry of Toluene, Mesitylene and Ethylbenzene[1,2,3]

BY ROBERT R. HENTZ[4] AND MILTON BURTON

Toluene, mesitylene and ethylbenzene are similar to benzene in their resistance to photochemical and radiation chemical destruction. Light absorbed in the 2537 A. region, presumably by the π-electron system, produces gas non-condensable at −120° with a quantum yield of the order of 10^{-4}. Quantum yields of molecules converted to polymer are roughly 16 times greater. The major primary photolysis occurs in bonds β to the ring with an additional small contribution from C–C bonds α to the ring. Atoms and radicals formed may add to a benzene ring, acquire a hydrogen atom from a methyl group in a molecule, or combine. Liquid state photolyses show considerable suppression of methane formation. Mercury-photosensitized decomposition of toluene and mesitylene gives low yields of hydrogen. In 1.8 mev. electron-induced radiolysis, 100 ev. yields of non-condensable gas range from 0.14 for toluene to 0.26 for mesitylene; *i.e.*, about 100 times greater than might be expected on a mere energetic basis by comparison with quantum yields. Radiolysis results are interpreted on the basis of energy absorption in either the ring or the side group, flow of energy from one to the other, and ensuant decomposition, the energy-yield of the latter being decreased by fluorescence from the π-electron system of the ring.

Studies of effects of high-energy electron irradiation have shown that aromatic hydrocarbons are markedly more resistant to decomposition than are other hydrocarbons.[5,6] In this work toluene, mesitylene, and ethylbenzene were chosen for study in the hope that differences in number and location of methyl groups and hydrogen atoms in the parent molecules would make possible some interpretation of the mechanism of their decomposition.

Analysis of the phenomena of radiation chemistry is complicated in part by the fact that two primary physical reactions are involved: excitation and ionization.[7] Detailed knowledge of the primarily excited states is presently lacking. Although it is usually said that they are essentially like those which may be excited by absorption of ultraviolet light, the fact is that electron bombardment may cause transitions forbidden in photon excitation. Nevertheless, the states obtained by electron bombardment probably behave similarly to those obtained in ordinary photochemistry, when due allowance is made, of course, for restrictions set up by selection rules governing transitions from those exceptional states which are not involved in photochemical processes.

Among pure aromatic compounds, benzene alone

---

(1) Paper presented before Division of Physical and Inorganic Chemistry, American Chemical Society, Chicago, September 5, 1950.

(2) Abstract of a thesis submitted by Robert R. Hentz to the Department of Chemistry of the University of Notre Dame in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(3) The Van de Graaff generator of the Chemistry Division, Argonne National Laboratory, was employed for some of the exposures described in this paper.

(4) Recipient of fellowships from Sinclair Refining Co. and E. I. du Pont de Nemours & Co.

(5) E. G. Linder and A. P. Davis, *J. Phys. Chem.*, **35**, 3649 (1931); C. S. Schoepfle and C. H. Fellows, *Ind. Eng. Chem.*, **23**, 1396 (1931).

(6) M. Burton, *J. Phys. Colloid Chem.*, **52**, 564 (1948).

(7) *Cf.* M. Burton, *ibid.*, **51**, 611 (1947); *Ann. Rev. Phys. Chem.*, **I**, 113 (1950).

seems to have received photochemical study.[8-12] There is no general agreement in published work other than that the quantum yield is very low. Studies in the photochemistry of pure toluene, mesitylene and ethylbenzene reported herein were performed as a necessary preliminary to, and integral part of, studies of their radiation chemistry.

Experimental

Chemicals.—A 500-ml. sample of Eimer and Amend, C.p. toluene, b.p. 110–111°, was fractionated in a theoretically 50-plate column. A constant-boiling middle fraction of 175 ml. was retained: n^{20}_{D} 1.4954; n^{20}_{D} (lit.) 1.4957.

A 250-ml. sample of Eastman Kodak Co. 546 mesitylene was fractionated and a constant-boiling middle fraction of 100 ml. was retained: n^{20}_{D} 1.4967; n^{20}_{D} (lit.) 1.4967.

A 500-ml. sample of Eastman Kodak Co. ethylbenzene was fractionated and a constant-boiling middle portion of 100 ml. was collected: n^{20}_{D} 1.4952; n^{20}_{D} (lit.) 1.4959.

The compounds purified as described were stored over sodium.

Light Sources.—The first light source used was a Hanovia Sc-2537 mercury resonance lamp which the manufacturer states gives 95% of its ultraviolet output in the 2537 Å. line. Use of this lamp proved unsatisfactory because of difficulty in elimination of mercury photosensitization. A Hanovia "L" burner was thereafter used for all photochemical exposures. It operates at 135 volts, 2.8 amp., 400°, and at a mercury vapor pressure of about 1 atm. A high intensity band spectrum with reversal of the resonance lines is obtained.

Photochemical Exposures.—In test of possibility of mercury photosensitization two sets of samples were employed. Mercury-contaminated samples were filled on a vacuum line using a mercury-diffusion pump and mercury measuring devices. Uncontaminated samples were filled on a vacuum line using an oil diffusion pump and completely free of mercury contamination. Contaminated samples exposed to the "L" burner gave results identical with those obtained on uncontaminated samples exposed to either the "L" or Sc-2537 lamps. On the other hand, contaminated samples exposed to the Sc-2537 gave characteristically different results interpretable as effects of mercury photosensitization. In consequence of these results, the "L" lamp was concluded to be satisfactory for photochemical studies without the necessity of maintaining completely mercury-free systems.

Photochemical exposures were made in quartz tubes of 15 mm. internal diameter equipped with graded seals and breakoffs. Sample tubes were filled on a vacuum line capable of giving a vacuum of 2×10^{-6} mm. of mercury, and were degassed by repeated cycles of freezing, pumping and melting. The length of vapor phase to be exposed was controlled by a shield of Pyrex tubing which fitted over the quartz tube and extended sufficiently above the liquid surface to prevent any light reaching the liquid phase. Liquid phase exposures were made with the vapor shielded in a similar manner.

Exposures of samples data for which appear in Table I were made at a temperature of 150–160° and at the vapor pressures of the materials at room temperature. In vapor phase runs the liquid in the bottom of the tube was maintained at room temperature. On the other hand, the heat of the "L" lamp was sufficient to maintain a temperature of 150–160° in an enclosed space and the vapor phase studies were consequently actually conducted at that temperature. At a distance of 3 cm. from the "L" lamp exposed samples yielded 10 to 20 micromoles of gas volatile at −120° in a period of 20 hours.

The quantum yield of liquid toluene was determined by comparison with a liquid ethyl iodide actinometer.[13] All other quantum yields were determined relative to liquid toluene. The reliability of the vapor-phase quantum yields is poor because of polymer accumulation on the walls and difficulty of insuring complete absorption.

To determine whether results observed in the case of toluene might be due to a small amount of 1849 Å. light, filters of 6% acetic acid and of cellophane, which do not transmit below 2000 Å., were employed in some runs. No differences in the effects were observed and the results are therefore attributed to the 2537 Å. region.

Electron Bombardments.—The electron bombardments were made on the Van de Graaff generators of the Physics Department of the University of Notre Dame and the Chemistry Division of the Argonne National Laboratory. A voltage of 1.80 mv. was used with currents of 2.0 to 2.5 microamp. for periods of 180 to 1500 sec.

The irradiation cell consisted of a Pyrex tube 15 mm. in i.d. and 2.5 cm. in length. A thin tungsten wire ran the length of the tube to within 1 mm. of a glass window of thickness of 0.014 to 0.018 in. A breakoff seal and a small tube for collection of gas products and transference of liquid were joined to the irradiation compartment.

Liquid to be bombarded was introduced into the irradiation compartment as described in the filling of the quartz tubes for photochemical studies. During irradiation, samples were cooled by a stream of running water. A grounded aluminum shield with a hole slightly smaller than the cell window ensured employment and measurement of only those electrons which entered the liquid and expended most of their energy in it. For electron current measurement, the tungsten lead in the reaction vessel was grounded through a low impedance and the current flowing therefrom to ground was registered by a Brown recording potentiometer. The area under the curves recorded by the Brown (giving the number of microcoulombs of charge passing through the sample) and the accelerating potential were measured to better than one per cent. The multiple of the two figures is taken as the total energy expended in the system including windows.

The energy expenditure in the chemical system was calculated therefrom by correction for loss in the thin glass windows. The range of 1.8 mev. electrons in g./cm.^{2} of aluminum was converted to range in cm. of glass by dividing by the density of glass (2.5 g./cm.^{3}). A linear rate of energy dissipation in glass was assumed and the energy dissipation in the cell window was taken as that fraction of the total energy given by the ratio of the window thickness (0.016 in.) to the range. Since the rate of energy dissipation is not linear, but smaller, when the electrons are at their maximum energy the value of 12% loss obtained in this manner is a maximum.

The data on yield are reported in terms of number of molecules produced or decomposed per 100 ev. of energy expended in the material. The symbol G is used for this quantity.[8,13a]

Product Analyses.—Products of exposures were separated into a gas fraction volatile at liquid nitrogen temperature, a gas fraction volatile at −120° (ethyl bromide mush) and a polymer. The gas analyses were performed in a semimicro gas analysis apparatus described by Saunders and Taylor.[14] These analyses were checked by mass spectrometric analyses on some samples. Gas analyses given are all averages of a rather large number (5 to 20) of separate determinations. In the worst cases, they are believed to be accurate within ±2 units (*e.g.* 10 ± 2%) of the values given; in most cases the accuracy is ±1 unit. Quantum yields have an accuracy of ±10% in the liquid phase. Vapor phase quantum yields given are roughly comparable to each other but are probably low. G values (*i.e.*, 100 ev. yields) given for radiolysis are precise within ±3% for toluene and ±10% for mesitylene and ethylbenzene.

In exposures of all three compounds studied both photochemical and radiation, the liquid becomes yellow-green in color. Pumping off the liquid leaves a yellow-green wax-like solid soluble in most organic solvents. Only the poly-

---

[8] J. R. Bates and H. S. Taylor, THIS JOURNAL, **49**, 2438 (1927).

[9] W. West, *ibid.*, **57**, 1931 (1935).

[10] G. S. Forbes and J. E. Cline, *ibid.*, **63**, 1713 (1941).

[11] G. I. Krassina, *Acta Physicochimica* (*U. R. S. S.*), **10**, 189 (1939).

[12] J. E. Wilson and W. A. Noyes, Jr., THIS JOURNAL, **63**, 3025 (1941).

[13] B. M. Norton, THIS JOURNAL, **56**, 2294 (1934).

[13a] NOTE ADDED IN PROOF. In all work subsequent to that reported in this paper a Leeds and Northrop Speedomax recorder has been used. We find that, for the particular operating conditions, the latter instrument indicates slightly higher average currents which are believed to be correct. All data presented here are appropriately corrected to the Speedomax base.

[14] K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

mer formed in toluene photolysis and radiolysis was examined in any detail. An estimate of the number of moles of toluene consumed in polymer formation was obtained by dividing the molecular weight of toluene into the weight of the waxy residue. The average molecular weight of the toluene polymer was found by the Rast method[15] to be 395 g./mole. Catalytic hydrogenation of the polymer with palladium-on-charcoal in the gas analysis system gave a value of only one aliphatic double bond per two molecules. The color, then, is not attributable to aliphatic conjugation. However, exposure of the material to air prior to the hydrogenations may have saturated some of the double bonds with oxygen.

Infrared studies on the toluene polymer yielded no information of interest other than the absence of characteristic absorption peaks of biphenyl, dibenzyl and oxygenated hydrocarbons.

Discussion and Results

Photochemistry.—Aromatic hydrocarbons begin to absorb in the neighborhood of 2700 Å. Absorption in this region is attributed to the π-electrons of the benzene ring. A 2537 Å. photon would put 112.5 kcal./mole of energy into the π electron system. However, since these compounds fluoresce strongly under such irradiation, any decomposition processes are in competition with fluorescence. Thus, a low quantum yield is to be expected.

The photochemistry of the group of compounds here reported may be discussed schematically in terms of the compound $R_2C_6H_3CH_2R$ where R may be either a methyl group or a hydrogen atom. We may write for the primary physical step in photochemistry

$$\mathrm{R_2C_6H_3CH_2R \xrightarrow{h\nu} R_2C_6H_3CH_2R^*}$$

Thereafter, both fluorescence and molecular deactivation may occur to a very important extent. Relatively speaking, chemical decomposition processes, which are nevertheless our present concern, make but a minor contribution to the total picture. For them we write

$$\mathrm{R_2C_6H_3CH_2R^* + R_2C_6H_3CH_2R \longrightarrow products} \quad (1)$$

$$\mathrm{R_2C_6H_3CH_2R^* \longrightarrow methylhexatriene\ biradical\ or\ analogs} \quad (2)$$

$$\mathrm{R_2C_6H_3CH_2R^* \longrightarrow R_2C_6H_2CH_2R + H} \quad (3)$$

$$\mathrm{R_2C_6H_3CH_3^* \longrightarrow R_2C_6H_3 + CH_3} \quad (4)$$

$$\mathrm{R_2C_6H_3CH_2R^* \longrightarrow R_2C_6H_3CHR + H} \quad (5)$$

with the additional possibilities peculiar to ethylbenzene

$$\mathrm{C_6H_5CH_2CH_3^* \longrightarrow C_6H_5 + CH_2CH_3} \quad (6)$$

$$\mathrm{C_6H_5CH_2CH_3^* \longrightarrow C_6H_5CH_2 + CH_3} \quad (7)$$

In mesitylene the primary ruptures would be the same as in toluene, but with different probabilities due to the differences in the number of bonds of the three types involved in (3), (4) and (5). Consider the probability that energy distributed in the π-electron system would transfer to a single bond in amount sufficient for a decomposition process. That probability should increase as the amount of energy required decreases. If this factor alone is involved, the lowest energy process should be favored. In toluene and mesitylene this is reaction (5). Szwarc[16] estimates a strength of 78 kcal./mole for this bond in toluene, whereas the strength of the bond involved in reaction (4) may be estimated to be about 85–90 kcal./mole and all other processes, except possibly the first, require over 100 kcal./mole. In ethylbenzene the weakest bond is that ruptured in reaction (7). Szwarc[17] estimates a strength of 63 kcal./mole for this bond.

In Table I, (*cf.* particularly footnote (*c*)) the data show that in toluene and mesitylene, in either liquid or vapor, reaction (5) is the predominant primary process. The quantum yields of hydrogen (% $H_2 \times \gamma$) in mesitylene as compared to toluene are consonant with a threefold greater probability of transfer of the required energy in mesitylene from the π-electrons of the ring to the hyperconjugated bonding electrons of the methyl groups. The small methane production in these two cases may come either from reaction (4) or from secondary reactions involving atomic hydrogen or from both. The relatively greater methane yield in mesitylene compared to toluene is also as might be expected. On the other hand, the relatively large yield of methane in the vapor phase photolysis of ethylbenzene compared to yields from toluene and mesitylene emphasizes the relative importance of reaction (7) in that case. The primary chemical process in the photolysis of all these compounds appears to be rupture of bonds β to the ring with little or no contribution from those α to the ring. However, for understanding of the sharp difference in yields in the two states, particularly in the case of ethylbenzene, some consideration of secondary reactions is required.

TABLE I

COMPARISON OF GAS COMPOSITIONS AND QUANTUM YIELDS IN PHOTOLYSES[a]

	H_2, %	CH_4, %	C_xH_y, %	$\gamma \times 10^4$
Liquid				
Toluene	93	3.2	4.1	1.1[b]
Mesitylene	89	6.8	4.0	3.8
Ethylbenzene	94	3.1	2.6	3.4
Vapor[c]				
Toluene	86	10.8	3.6	0.6
Mesitylene	84	8.7	7.0	1.7
Ethylbenzene	14	50	36	1.4
Toluene polymer				9.6[d]

[a] Comparison runs made at a temperature of 150° and vapor pressures of 1–10 cm. [b] Number of moles of gas produced volatile at −120° per einstein absorbed. [c] Quantum yield data in the vapor phase have only rough relative reliability. Very definitely, they are not to be compared with data for the liquid phase. At best, they are rough even among themselves and are most likely lower than the true values. [d] Number of moles of toluene decomposed to polymer per einstein absorbed, determined by dividing the weight of polymer formed per einstein absorbed by the molecular weight of toluene.

Possible secondary reactions of atoms or radicals formed in the primary process and some of their approximate activation energies in kcal./mole are

$$\begin{array}{lll} & E_a & \\ \mathrm{R_2C_6H_3CH_3 + CH_3 \longrightarrow R_2C_6H_3 + C_2H_6} & \approx 30 & (8a)^{18} \\ \mathrm{R_2C_6H_3CH_3 + H \longrightarrow R_2C_6H_3 + CH_4} & \approx 30 & (8b)^{18} \\ \mathrm{R_2C_6H_3CH_2R + R \longrightarrow R_2C_6H_2CH_2R + RH} & >10 & (9)^{19} \end{array}$$

---

[15] E. B. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936).

[16] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

[17] M. Szwarc, *ibid.*, **17**, 431 (1949).

[18] *Cf.* The calculation of E. Gorin, W. Kauzman, J. Walter and H. Eyring, *ibid.*, **7**, 633 (1939) for the case of $H + CH_4 \rightarrow CH_4 + H$.

[19] *Cf.* J. C. Smith and H. S. Taylor, *ibid.*, **8**, 543 (1940).

$$R_2C_6H_3CH_2R + CH_3 \longrightarrow R_2C_6H_3CHR + CH_4 \quad 5.6 \quad (10a)^{19}$$

$$R_2C_6H_3CH_2R + H \longrightarrow R_2C_6H_3CHR + H_2 \quad (10b)$$

$$R_2C_6H_3CH_2R + R \longrightarrow R_3C_6H_3CH_2R \text{ (radical) small} \quad (11)$$

$$R + R + M \longrightarrow R_2 + M \quad \sim 0 \quad (12)$$

and for the special case of ethylbenzene

$$C_6H_5CH_2CH_3 + CH_3 \longrightarrow C_6H_5CH_2 + C_2H_6 \quad (13)^{18}$$

$$C_6H_5CH_2CH_3 + H \longrightarrow C_6H_5 + C_2H_6 \quad (14a)$$

$$C_6H_5CH_2CH_3 + H \longrightarrow C_6H_5CH_2 + CH_4 \quad (14b)^{18}$$

In Table I the fraction C_xH_y is, as nearly as can be told from mass spectrometric analysis, 100% ethane. Relatively low yield of hydrogen and relatively large yields of ethane and methane in vapor phase photolysis of ethylbenzene in contrast to toluene and mesitylene are consistent with the great probability of reaction (7) as compared to (5) or to (6). Of all the reactions which could yield ethane careful consideration indicates that it is most likely formed *via* reaction (12) from methyl radicals originating in reaction (7).

Regarding specific reactions of atomic hydrogen Bonhoeffer and Harteck[20] and Geib and Harteck[21] have found that the addition of hydrogen atoms to a benzene ring (*cf.* reaction (11)) occurs readily. Forbes and Cline[10] have found that irradiation of mixtures of mercury vapor, hydrogen and benzene with light of a mercury-vapor resonance lamp induces disappearance of hydrogen. They attribute this effect to dissociation of hydrogen by excited mercury atoms and subsequent absorption of hydrogen atoms by the benzene ring. They found cyclohexadiene and hydrogenated biphenyls among the products.

In summary, free atoms and radicals most likely disappear by reactions (10), (11) and (12), reactions (10) and (12) giving rise to the main gas products observed and the radical formed in (11) leading to polymer formation and possibly some methane and ethane in subsequent decomposition of the large radical.

Data in Table I on the photochemistry of the liquid state may be taken as evidence for a free radical process. In terms of the Franck–Rabinowitch[22] hypothesis, primary recombination of large fragments can be responsible for the apparent trend toward suppression of methane and ethane formation. The smaller hydrogen atoms may escape through the sheath of surrounding molecules in the liquid phase and no decrease in the quantum yield for hydrogen formation should be expected. The fluorescence of aromatic hydrocarbons in all three states of aggregation indicates that collisional deactivation makes but little contribution to decrease of quantum yield in the liquid phase. In concluding this section we note that in the special case of ethylbenzene the rearrangement process

$$C_6H_5CH_2CH_3^* \longrightarrow C_6H_5CH{=}CH_2 + H_2 \quad (15)$$

may be of considerable importance.

Mercury Photosensitization.—Table II shows that, in presence of mercury, exposure of toluene and mesitylene to the Sc-2537 lamp at vapor pressures high enough to give fifty per cent. absorption in 3–5 mm. of path gives approximately the same results as those obtained in unsensitized photochemical studies. At the low vapor pressures, the products consist almost wholly of methane. This result may be attributed to an absorption competition between the organic molecule and mercury vapor; the low vapor pressure absorption could be predominantly by mercury vapor and the results would then arise mainly from a mercury-photosensitized reaction.

TABLE II

COMPOSITIONS OF GASEOUS PRODUCTS IN PHOTOLYSES WITH THE Sc-2537 LAMP COMPARED WITH APPROXIMATE RECIPROCAL ABSORPTION[a]

	Reciprocal absorption	H_2,%	(CH_4 + C_xH_y), %
Mesitylene	42	0.6	99.4
Toluene	69	11.8	88.2
Mesitylene	3	89.0	11.0
Toluene	5	83.2	16.8

[a] The reciprocal absorption is expressed in terms of the number of millimeters of path required for 50% absorption. This is calculated from the Beer–Lambert law using the value of 0.45 for the optical density of toluene vapor at 13.8 mm. pressure and 25° in a cell 5.0 cm. in length. This value was obtained from data in the American Petroleum Institute Reports. The same value is used for mesitylene.

In this reaction primarily formed hydrogen disappears by mercury-photosensitized reaction with the aromatic molecule, as found by Forbes and Cline.[10] Consequently, the only final products are methane and polymer. Methane may arise from a ring rupture process or from rupture of the methyl to phenyl bond. Finding of 40% methane in the products of the mercury photosensitization of benzene by Bates and Taylor[8] indicates possibility of a major contribution by the ring rupture mechanism.

Radiation Chemistry.—Under high-energy radiation excited molecules result from both primary and secondary physical processes. Energies available are sufficient, and the mechanism is such as to permit excitation or ionization of any electron in the molecule. When a positive ion results, as in the latter process, it is ultimately neutralized and a highly excited particle is produced.[6,7] In the case of aromatics there is some reason to believe that most such neutralization processes yield the parent molecule in an excited state.[23,24]

Table III indicates the results obtained on electron bombardment of the three liquids studied.

TABLE III

RESULTS OF ELECTRON IRRADIATIONS OF LIQUIDS

	G[a]	H_2, %	CH_4, %	C_xH_y, %
Toluene	0.14	93	5.7	1.0
Mesitylene	.26	92	6.9	0.8
Ethylbenzene	.21	84	14.2	2.0
Toluene polymer	1.28			

[a] The number of molecules of gas produced volatile at −120° per 100 ev. absorbed, except for toluene polymer where it is the number of molecules of toluene converted to polymer (determined by dividing weight of polymer by the molecular weight of toluene).

---

[20] K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **139** (Haber Band), 64 (1928).

[21] K. H. Geib and P. Harteck, *Ber.*, **68**, 1815 (1933).

[22] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[23] M. Burton, *Proc. Conference on Nuclear Chem., Chem. Inst. Canada*, 179 (1947).

[24] J. L. Magee and M. Burton, THIS JOURNAL, **72**, 523 (1950).

The comparisons in Table IV of the data in Table III show a fair correlation between relative G values for gas yields and relative numbers of bonds of a given type external to the benzene ring in the three molecules studied. A perfect correlation might indicate that all radiolytic effects of any magnitude are the consequence of primary physical effects in the side groups exclusively. However, ethylbenzene shows a much higher G'_{CH_4} as compared with B'_{C-C} (3.74 to 2.00) than can be accounted for on such a basis. The implication in such a case is that the contribution from primary physical processes in the ring (*cf.* vapor photolysis) cannot be neglected. In the mesitylene case the contribution of excitation of the ring shifts the $G'_{H_2}:B'_{C-H}$ ratio in the same direction.

TABLE IV

COMPARISON OF RELATIVE G VALUES FOR GAS PRODUCTION WITH THE RELATIVE NUMBER OF CORRESPONDING BONDS EXTERNAL TO THE BENZENE RING IN THE PARENT MOLECULE

	G'_t[a]	B'_t	G'_{H_2}	B'_{C-H}	G'_{CH_4}	B'_{C-C}
Toluene	1.00	1.00	1.00	1.00	1.00	1.00
Ethylbenzene	1.50	1.33	1.36	1.25	3.74	2.00
Mesitylene	1.86	1.67	1.84	1.50	2.25	3.00

[a] G'_t is the G value for total gas production relative to that in toluene as unity. The other G's have a corresponding significance. B'_t is the ratio of the total number of bonds external to the benzene ring in the given molecule to that in toluene. The other B's have a corresponding significance for the number of hydrogen to carbon bonds and carbon-to-carbon bonds.

An Interpretation.—In radiation chemistry much of the excitation is ensuant on primary ionization. Such excited molecules, which may ultimately decompose, possess energy considerably in excess of that required for bond rupture. Radicals resultant from such decomposition can have so much kinetic energy that they escape the cage of surrounding molecules without recombination. Consequently, as a first approximation, radiolysis even of liquids should be compared to photolysis of vapors.

However, the picture for these compounds should not be oversimplified. In their radiolysis initial, or early, excitation occurs both in the ring and in the side group. In their photolysis, in the wave length range employed, only the ring is initially involved. The comparison is therefore limited.

Furthermore, some excitation in radiolysis occurs in a primary physical process; *i.e.* at relatively low energy levels characteristic of photolysis. For that portion of such excitation which occurs in the ring the proper comparison is to the photolytic behavior of the same substances in the same state (*i.e.* the liquid state in these cases). On the other hand, where primary radiolytic excitation is in the side group, no comparison to the photochemical studies here reported is proper.

The treatment would be better if vapor phase radiolytic data were presently available but unfortunately they are not.

With these restrictions acknowledged, we may still propose a reasonable picture of the radiolysis. Relative amounts of energy initially localized in the ring (essentially in the π-electron system) and in groups external to the ring are roughly proportional to numbers of electrons in the two locales. On such basis most of the energy is initially absorbed in the ring but the contribution from initial energy absorption in the side groups increases with size and number of groups (*cf.* Table IV). When energy is initially absorbed in the ring, much of it is lost by fluorescence and the chemical effect is small (*cf.* quantum yields, Table I). However, this effect is decreased in radiolysis when the initial process is ionization because of the large excess energy involved (note comparison of liquid radiolysis to gaseous photolysis). On the other hand, some of the energy is transferred out of the ring and causes decomposition of side groups (*cf.* photolysis). To some extent this destructive transfer of energy out of the ring is compensated by flow of energy initially localized in the side group into the ring, where it may be lost by fluorescence. The evidence for this latter phenomenon lies in the fact that radiolytic yields of decomposition products from these alkyl substituted aromatic compounds are so much lower than from pure alkanes.[5,23]

It is interesting to note that the quantum yield of 10^{-4} obtained in the photochemistry corresponds to a G value of about 2×10^{-3}. The radiation chemistry process is more efficient by a factor of 100. This result may be due either to an increased probability of the decomposition processes relative to fluorescence because of the higher energies involved, to the more efficient bond rupture excitations in the bonds external to the benzene ring, to a greater efficiency of ionic processes, or to any or all of the three effects.

NOTRE DAME, INDIANA RECEIVED JULY 20, 1950