$$4NH \xrightarrow{W} NH_4N_3 \qquad (7)$$

They specifically note an inability to detect free NH in the electric discharge through ammonia even at low pressure. Unfortunately, there does not appear to be any direct evidence of reaction or absence of reaction in the gas phase between NH radicals, *i.e.*

$$NH + NH \longrightarrow N_2 + H_2 \qquad (8)$$

or between NH radical and some other molecule such as NH_3 or N_2H_4. Reaction 6 has a formal similarity to $CH_2 + H_2 \xrightarrow{M(?)} CH_4$, which appears to be rather well established.[6a,24]

Reactions between NH and NH_2 radicals are ruled out by the fact that the yields of N_2 and N_2H_4 (the products of the presumed reactions 2 and 5 or 8) are not interdependent (*cf.* section 4.1.7).

The catalytic effect of platinum walls on hydrazine formation suggests the importance of a reaction which can interrupt the back reaction, 2 or 4, *e.g.*,

$$H + H \xrightarrow[\text{or W}]{M} H_2 \qquad (9)$$

The effect of platinum walls is explained most simply by increase in the rate of reaction 9 and consequent decrease in rate of reaction 4.

4.5 Hydrazine Decomposition.—Hydrazine is rapidly destroyed in the discharge and nitrogen is not formed in this process (section 4.1.3). Steady-state concentrations were established at values less than 0.1 mole per cent. in the platinum-coated tube. The lowest excited state of hydrazine is probably triplet and the lowest significant excited state probably corresponds to the dissociation energy of the $H_2N–NH_2$ bond. This figure is given by Szwarc[25] as ~2.6 e.v. in rather good agreement with a value of 2.9 e.v. estimated from the 4.65 e.v. value of the $H–NH_2$ bond. Neglecting considerations of possible difference in cross-sections for the electronic interactions and assuming, as before, that the average electron temperature is about 1.4 e.v., it follows that the probability of production of $N_2H_4^*$ is at the most about 5 times that of attainment of path I. Thus, preferential excitation of N_2H_4 would not appear to be the limitation responsible for the relatively low concentration of hydrazine (*e.g.*, ~0.04 mole per cent. in Table I, run 56) obtain in this work, so that reaction 4 rather than reaction 3 would appear to be the major restriction on yield and steady-state concentration of hydrazine. This conclusion is contrary to the view of Ouchi.[4b]

4.6 Reaction in the Negative Glow.—Whether production of inappreciable quantities of hydrazine in the negative glow is due to its rapid destruction or to its substantial lack of formation in this region is not known. The average energy near the cathode edge is probably higher, while that near the anode edge lower, than that existing in the positive column.[5d] Evidence has been presented that at high flow rates some hydrazine does escape from this region.

The data in A.D.I. Tables 2 to 4 indicate a maximum energy efficiency for nitrogen production in the negative glow between 2 and 3 mm. pressure with a value approximately equal to that in the positive column at high pressures. The paucity of data available on the reaction and on the electron energy distribution in this region[4e,f,g] forbid discussion of mechanism. The situation is further complicated by the possibility that reactions occur in the Faraday dark space.[4c]

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[24] C. E. H. Bawn and J. Milstead, *Trans. Faraday Soc.*, **35**, 889 (1939).

[25] *Cf.* M. Szwarc, *Chem. Revs.*, **47**, 75 (1950). If a low NH bond dissociation energy is assumed for NH_3 (*cf.* footnote 14) the agreement is better.

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

Polymer Production in Radiolysis of Benzene[1,2]

BY W. N. PATRICK AND MILTON BURTON

RECEIVED JANUARY 4, 1954

Irradiation of liquid benzene with 1.5 Mv. electrons gives polymer as a non-volatile product with a 100 e.v. yield $G(C_6H_6 \rightarrow \text{polymer}) = 0.75$ independent of intensity and total energy input. Average molecular weight increases non-linearly with energy input; the maximum value observed was ~530. At the same time G(double bond formation) decreases linearly with input independent of intensity. In explanation of the results it is suggested that a fixed fraction of the primarily excited benzene molecules are excited to a particular energy level and then react to give polymer formation.

1. Introduction

Polymer is produced in electron-bombardment radiolysis of benzene with a 100 e.v. yield of benzene molecules converted to polymer, *i.e.*, $G(C_6H_6 \rightarrow \text{polymer})$, previously given as 0.76.[3] Little, however, has been published about its production or its nature. Such information, useful perhaps for elucidation of the mechanism of radiolysis of benzene and for clarification of some details of behavior of benzene mixtures, is presented in this report.

2. Experimental

The benzene used in this work was a portion of an exceptionally high-purity sample[4] previously employed in synthesis of benzene-d_6. Techniques of irradiation by 1.5 Mv. electrons are largely those described in an earlier paper.[4] However, for determination of polymer, the irradiation cells were necessarily modified by extension of the

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[1] A contribution from the Radiation Project operated by the University of Notre Dame and supported in part by the Atomic Energy Commission under Contract AT(11-1)-38.

[2] Abstract from a thesis presented to the Department of Chemistry of the University of Notre Dame by W. N. Patrick in partial fulfillment of requirements for the degree of Doctor of Philosophy.

[3] J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

[4] W. N. Patrick and M. Burton, *ibid.*, **58**, 424 (1954).

reservoir with a length of 8 mm. tubing. Although the total volume of liquid was ~ 4.8 ml., the irradiated volume was <1 ml.

After irradiation, the benzene was slowly distilled off under vacuum leaving a yellow viscous polymer on the walls of the extension tube. The benzene was distilled back into the tube by means of liquid nitrogen and frozen on its walls. On thawing, the benzene then washed the polymer down to the bottom of the tube and was distilled off. The 8 mm. tube containing the polymer was thereafter broken off and quickly weighed.

The polymer was dissolved in CCl_4 for determination of aliphatic double bonds by bromine addition.[5] Benzene "double bonds" are not shown by this method. The average molecular weight of the polymer was determined by the lowering of the melting point of camphor.[6] One set of polymer samples, sealed under vacuum, was sent to Micro-Tech Laboratories of Skokie, Illinois, who performed the carbon and hydrogen determinations herein reported. Infrared spectra were run on a Baird I. R. Spectrophotometer.[7]

3. Results

The non-volatile fraction left as a yellow residue when the irradiated benzene was distilled out of the containing tube under high vacuum is indiscriminately called polymer. It was definitely not a single substance. The viscosity, for example, was a function of the total amount of energy expended per unit volume of irradiated sample; such conclusion followed simple visual observation of the rate of flow of the residue. Samples from short irradiation were oily and relatively fluid; larger doses yielded heavier grease, deeper in color.

The last of the volatile liquid was always driven off by heating with an infrared lamp to the boiling point of the polymer under a high vacuum. Prolonged heating of the polymer did not appear to change its viscosity. However, a small amount of white solid distilled out and settled on the cooler parts of the tube. This white solid, insufficient for isolation for physical measurements, could be distilled back and forth with application of very little heat. It is believed to be biphenyl (m.p. 69–71°, b.p. 254–50°), presence of which in irradiated benzene has been previously indicated.[8]

Prolonged heating of the polymer at the bottom of the tube caused various fractions to distil up its sides. These appeared as a light oil half-way up the tube, gradually increasing in viscosity down the side to a heavy polymer at the bottom. Evidently, the polymer was not a single compound but varied in composition from a unit of two benzene rings joined together to heavier, more complicated structures.

Measurements of physical properties of the polymer all entailed some exposure of samples to the atmosphere. However, the infrared spectra of the polymer showed an important contribution of aromatic nuclei but no absorption peaks characteristic of the carbon–oxygen bond in alcohols, aldehydes, ketones, acids or acid anhydrides. Apparently, little atmospheric oxidation occurred.

Weighing of the polymer for yield and molecular weight determinations was accurate only within about 10%, for the samples weighed about 0.06 g. The determination of G(double bonds), the number of double bonds produced per 100 e.v. expended in the sample, was probably much more accurate since the results did not depend on weighing but on volumetric technique.

The average molecular weight was determined only for samples of mixed polymer, not for any single fraction. Figure 1 shows that the average molecular weight increases with total energy input, that the rate of increase drops off with increased dosage, and that limited variation of intensity of exposure has no effect on the result. The top molecular weight measured corresponds to an average of slightly less than seven molecules of benzene per molecule of polymer. One might expect the curve to extrapolate to molecular weight 154 (*i.e.*, biphenyl) at zero time. However, Gibson, Blake and Kalm[9] have shown that in the photolysis of benzene in glassy solution at low temperature an early product is probably *trans*-hexatriene. Thus it is possible that this latter compound may be present as a precursor of the polymer observed and that the extrapolated zero-time molecular weight should be somewhat less than 154. Table I shows that over the entire range of dosage and intensity the H–C ratio in the polymer is equal to, or slightly exceeds, unity, as it should if the hexatrienyl radical is involved in polymer formation.

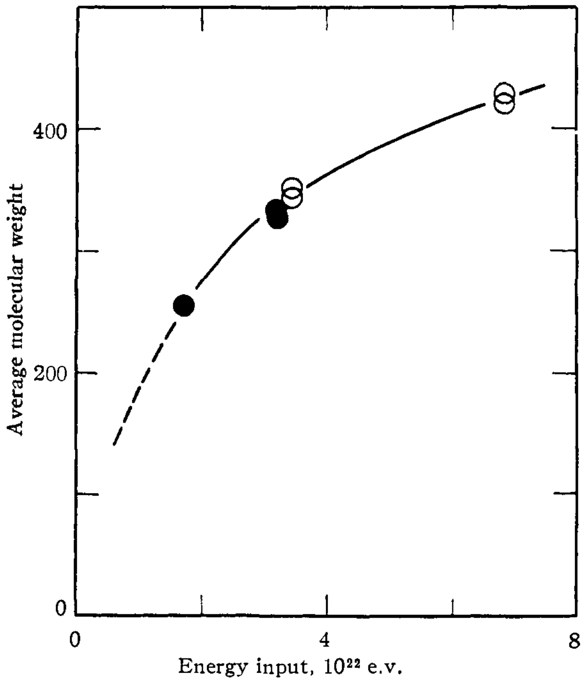

Fig. 1.—Average molecular weight of polymer formed by irradiation of benzene as a function of energy input.

Table II shows that, over the range of exposure studied, the number of molecules of benzene converted to polymer depends only on the dosage. The average value $G(C_6H_6 \rightarrow \text{polymer}) = 0.75$ in good

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(5) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 33.

(6) F. Daniels, J. H. Mathews, J. W. Williams, *et al.*, "Experimental Physical Chemistry," Fourth Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 81.

(7) The authors express their grateful appreciation to Mr. A. V. Verbiscar for coöperation in these determinations.

(8) R. Schlegel, "National Nuclear Energy Series," Div. 4, Vol. 10B, Paper 1.3 (1946).

(9) G. E. Gibson, N. Blake and M. Kalm, *J. Chem. Phys.*, **21**, 1000 (1953).

TABLE I

CARBON AND HYDROGEN ANALYSES OF THE POLYMER OBTAINED FROM C_6H_6 UPON IRRADIATION WITH 1.5 M.V. ELECTRONS

Current, µamp.	Irradiation time, min.	Wt. % C	Wt. % H	Ratio H/C
2.2	15.1	92.11	7.84	1.02
2.2	30	92.01	7.68	1.00
2.2	45	92.21	7.76	1.01
2.2	60	92.43	7.70	1.00
1.1	90	92.17	7.81	1.02
1.1	30	91.93	8.00	1.04

agreement with the value ~0.76 of Manion and Burton,[3] based on somewhat less extensive data.

TABLE II

POLYMER YIELD FROM IRRADIATION OF BENZENE WITH 1.5 M.V. ELECTRONS

Energy input, e.v. × 10^{-22}	Current, µamp.	Irradiation time, min.	$G(C_6H_6 \rightarrow \text{polymer})$
6.68	2.2	60	0.768
6.44	2.2	60	.736
6.52	2.2	60	.773
6.54	2.2	60	.804
6.82	2.2	60	.735
3.42	2.2	30	.727
1.72	1.1	30	.697
3.20	1.1	60	.777
3.28	2.2	30	.749
3.24	1.1	60	.742
6.74	1.1	120	.752
		Average	.75

Figure 2 summarizes the data on double bond formation. The value G(double bonds) is the measured number of double bonds produced per 100 e.v. of energy expended in the benzene.

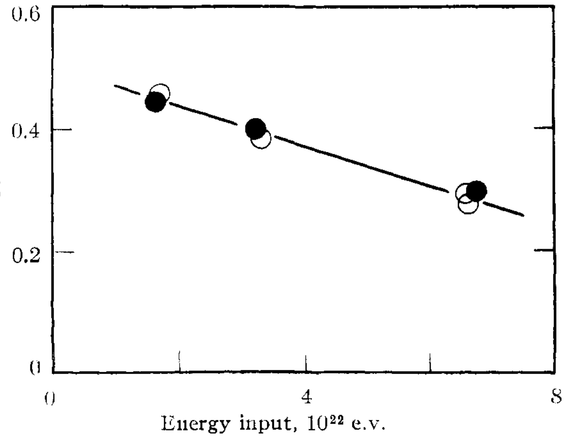

Fig. 2.—Variation of 100 e.v. yield of double bonds with energy input into liquid benzene.

4. Discussion

The results clearly show that the process of polymer formation involves first the formation of double bonds and then their gradual disappearance as the polymer aggregate increases in size. Production of HD in radiolysis of a mixture of benzene and benzene-d_6 seems to indicate the reality of the mechanism[10]

$$C_6H_6 \rightsquigarrow C_6H_6^* \qquad (1a)$$

$$C_6H_6^* \longrightarrow C_6H_5 + H \qquad (1b)$$

as an important feature of the decomposition. If the free H atom does not escape by the combination reaction $H + H \rightarrow H_2$ or by the back reaction[11] $C_6H_5 + H \rightarrow C_6H_6$, its most probable fate seems to be

$$C_6H_6 + H \longrightarrow C_6H_7 \qquad (2)$$

According to Geib and Harteck the reaction of H atoms[12] with benzene at liquid air temperatures yields a partially hydrogenated benzene mixture. This result is in general agreement with the evidence for *trans*-hexatriene formation in low-temperature photolysis of glassy benzene solutions.[9] It appears from other evidence that, although H atoms react with benzene vapor at higher temperature they do so without formation of cyclohexane or cyclohexadiene.[13] Forbes and Cline, however, did find evidence for cyclohexadiene formation.[14] The work of Melville and Robb[15] indicates that reaction 2 has nearly zero activation energy in the vapor state.

Work on radiolysis of a liquid mixture of propionaldehyde and benzene-d_6 indicates that reaction 2 may be the precursor of H_2 formation, by the reaction

$$C_6H_7 \longrightarrow C_6H_5 + H_2 \qquad (3)$$

as well as of polymer formation by some not clearly defined process.[4] Under conditions of considerably less total energy input (*i.e.*, photolysis), Gibson, Blake and Kalm[9] obtained hexatriene formation. It must be remembered that under their conditions of relatively long-wave irradiation (2400–2600 Å.) H_2 formation has never been observed.[16] Consequently, they proposed a mechanism involving triplet-excited benzene produced in the primary excitation

$$C_6H_6 \xrightarrow{h\nu} C_6H_6^* \qquad (1c)$$

Such excited benzene in their picture successively extracts H atoms from the frozen donor solvent

$$C_6H_6^* + RH \longrightarrow C_6H_7 + R \qquad (4)$$

with ultimate formation of C_6H_8, *trans*-hexatriene.

We suggest that in our work on liquid benzene certain of the freely-moving excited benzene molecules react with any available free radical, *e.g.*, phenyl, C_6H_7 (probably hexatrienyl according to the ideas suggested by the work of Gibson, Blake and Kalm[9]), H or some more complicated entity

$$C_6H_6 + R \longrightarrow R{\cdot}C_6H_6 \qquad (5)$$

to give a free radical polymer whose growth is ultimately terminated by combination with another free radical

$$R(C_6H_6)_n + R \longrightarrow R(C_6H_6)_nR \qquad (6)$$

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(10) S. Gordon and M. Burton, *Faraday Soc. Disc.*, No. 12, 88 (1952).

(11) Reasons for rejection of the back reaction as an important factor in decrease of yield are given by M. Burton, *Proc. Conf. on Nuclear Chem., Chem. Inst. of Canada*, 179 (1947).

(12) K. G. Geib and P. Harteck, *Ber.*, **66**, 1815 (1933).

(13) H. I. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951).

(14) G. S. Forbes and J. E. Cline, THIS JOURNAL, **63**, 1713 (1941).

(15) H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* (*London*), **A202**, 181 (1950).

(16) *Cf.* J. E. Wilson and W. A. Noyes, Jr., THIS JOURNAL, **63**, 3025 (1941); G. I. Krassina, *Acta Physicochimica* (*U.S.S.R.*), **10**, 189 (1939).

According to Table I, the H/C ratio in the polymer is only slightly above unity, tending perhaps to be greatest for the smallest energy inputs. The mechanism suggested is consistent with such a result. Hydrogen produced as by reaction 3 would ultimately be balanced by production of an approximately equivalent amount of biphenyl.

As an alternative mechanism we may consider the possibility of a reaction like

$$C_6H_6^* + C_6H_6 \longrightarrow (C_6H_6)_2 \qquad (6a)$$

The dimer can be a radical and can add either to other normal benzene molecules in a relatively slow reaction or much more rapidly by the general process

$$(C_6H_6)_n + C_6H_6^* \longrightarrow (C_6H_6)_{n+1} \qquad (7)$$

It is required for reactions such as 7 that the excited molecule $(C_6H_6)^*$ be stable, even though reactive. Evidence for such stability has already been recounted.[16] A formally similar reaction has been postulated to account for certain peculiar features of the radiolytic polymerization of acetylene.[17]

An important feature which must be explained by any suggested mechanism for polymer formation is that $G(C_6H_6 \rightarrow \text{polymer})$ is independent both of intensity within a factor of two and of total energy. One might be tempted to associate this result with the constancy of $G(H_2) \sim 0.036$ over a great range of energy output and intensity,[3] but the fact is that $G(C_6H_6 \rightarrow \text{polymer})$ remains constant although G(double bonds) and the average molecular weight of polymer are both greatly dependent on total energy input but not on intensity. A satisfactory interpretation is that the initially excited benzene molecules which react inevitably to give polymer are those which are excited with a fixed probability to a definite energy level; the number of these molecules considerably exceeds those which are primarily decomposed to give hydrogen.

Although we have no clear-cut mechanism for formation of benzene polymer we are left with the conclusion that H atoms are not involved to an important extent.

It remains to speculate briefly about the nature of the polymer produced. Consider, for example, the polymer which contains an average of five molecules of benzene. According to Figs. 1 and 2 such an "average molecule" contains an average 0.6 double bond per benzene ring or about 3 double bonds per unit of polymer. A little experimentation will convince the reader that it is possible to draw several such "average molecule" structures, in which six-membered rings are attached to a partially saturated chain of the type suggested by the work of Gibson, Blake and Kalm.[9] However, in the present stage of our information it is not possible to make adequate test of such a structure against results or even to establish that such an "average molecule" is at all present in the polymer.

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[17] J. L. Magee and M. Burton, *J. Phys. Chem.*, **56**, 842 (1952).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE CATHOLIC UNIVERSITY OF AMERICA]

The Thermal Decomposition of Acetaldehyde[1]

BY FRANCIS OWEN RICE AND ROBERT E. VARNERIN

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When 50-50 mixtures of $CH_3CHO-C_2D_6$ or $CD_3CDO-C_2H_6$ are decomposed, the amount of isotopic mixing as measured by the CH_3D/CH_4 or CD_3H/CD_4 ratios is proportional to the fraction of aldehyde decomposed. When different amounts of NO are added to the aldehyde-ethane mixtures the ratios of CH_3D/CH_4 or CD_3H/CD_4 are (for constant fractional decomposition of the aldehyde) either independent of the concentration of NO or increase somewhat as the NO concentration increases. When 50-50 mixtures of $CD_3CDO-CH_3CH{=}CH_2$ and $CD_3CDO-C_2H_6$ are decomposed, the CD_3H/CD_4 ratio for a given fractional decomposition of aldehyde is 1.8:1 respectively for the two reactions. Our results indicate (1) that the thermal decomposition of CH_3CHO and CD_3CDO are similar, (2) that both are chain reactions unaccompanied by any significant amount of direct separation into product molecules and (3) that the thermal decomposition of a substrate in presence of an indicator (in which either the substrate or indicator is fully deuterated) provides a general method for studying elementary reactions.

1. Introduction

The thermal decomposition of acetaldehyde is a homogeneous reaction that proceeds at a measurable rate at about 500° according to the equation $CH_3CHO \rightarrow CH_4 + CO$, with almost complete absence of any complicating simultaneous reactions. Although the facts regarding the over-all change are not in dispute, the situation is very different with regard to the detailed mechanism. This may occur intramolecularly by migration of a hydrogen atom or by rupture of a carbon-carbon bond followed by a chain reaction such as suggested by Rice and Herzfeld.[2] Since the evidence for and against these views has been adequately summarized[3] we shall mention here only those aspects having a direct bearing on our own experiments.

In the thermal decomposition of acetaldehyde the presence of small quantities of NO (less than 1.0 mm.) has no appreciable effect on the rate if the initial aldehyde pressure is about 150 mm. but reduces the rate appreciably when the initial aldehyde pressure is about 50 mm.[4] For pressures of NO higher than about 2 mm. there is always a marked

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[1] This research was supported by the United States Air Force under contract no. 18(600)-64 monitored by the Office of Scientific Research.

[2] F. O. Rice and K. H. Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, pp. 120-129; C. N. Hinshelwood, "Kinetics of Chemical Changes," Clarendon Press, New York, N. Y., 1947, pp. 137-139.

[4] (a) L. A. K. Staveley and C. N. Hinshelwood, *J. Chem. Soc.*, 813 (1936); (b) J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 246 (1942).