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THE ELECTRON RADIOLYSIS OF BENZENE-BIPHENYL MIXTURE

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ABSTRACT

Mixtures of benzene (also perdeuterobenzene) and biphenyl were irradiated with 6 MeV electrons. The primary polyphenyl products were biphenyl; o-, m-, and p-terphenyls; o,o-, m,m-, p,p-, o,m-, o,p-, and m,p-quaterphenyls. A mechanism is proposed which accounts for the initial distributions of these individual products. The basic radiolytic reaction is divided into two general parts (radical production and radical scavenging). A mathematical treatment is used to derive radical and scavenging probabilities. A close parallel was noted between free radical chemistry and these electron radiolytic studies.

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THE ELECTRON RADIOLYSIS OF BENZENE-BIPHENYL MIXTURES

I. INTRODUCTION

It has been demonstrated that the initial principal high boiler products obtained from the electron radiolysis of biphenyl are the six linear quaterphenyls [1]. This paper presents a quantitative description of the radiation chemistry and mechanism of initial polyphenyl production from benzene-biphenyl mixtures. The relative polyphenyl product yields were used to calculate partial rate factors for radiolytic reactive species generation and partial rate factors for the scavenging of these reactive species by the parent molecules. The general approach used was similar to that of Hutchinson et al [1] and was extended to include aromatic mixtures. This paper provides a mathematical foundation for further study of the radiolysis of polyphenyl mixtures which are important in organic cooled reactors.

It was noted that partial rate factors for the scavenging reactions (substitution reactions) are in general agreement with those in the literature of free radical chemistry [2, 3]. Partial rate factors for the radiolytic generation of reactive species were reported by Hutchinson et al for biphenyl; however, this paper appears to be the first application of partial rate factors to the radiolytic generation of reactive species in binary mixtures.

Isotope effects were measured by comparing the radiolysis of benzene-biphenyl and perdeuterobenzene-biphenyl mixtures. These radiolytic reactions were allowed to proceed only long enough to obtain measurable amounts of products. It was not the purpose of these studies to measure the rates of production and destruction of the individual polyphenyl products, but to measure their initial relative yields. Mole fraction yields were used as a matter of convenience in the probability calculations which were made.

II. EXPERIMENTAL

The benzene-biphenyl mixtures were placed in glass ampoules and degassed by a series of melt, freeze, and evacuation steps (0.05mm). The samples were irradiated for approximately three hours at 80°C., using 6 MeV (average) electrons from an Applied Radiation Corporation linear accelerator. Approximately one to two percent of the reactants was converted to polyphenyl products. The product analyses were completed using gas-solid chromatographic techniques [4] where the irradiated samples were compared to known materials.

Benzene tagged with carbon-14 was used in one of the mixtures to determine the amount of biphenyl produced from benzene in an equal molar benzene-biphenyl mixture. The biphenyl was separated from the products by sublimation. The amount of carbon-14 tagged biphenyl was determined using a Baird-Atomic, Inc., Model 245, liquid scintillation counter.

III. RESULTS AND DISCUSSION

The principal high boiler polyphenyl products were biphenyl; o-, m-, and p-terphenyls; o,o-, m,m-, o,m-, o,p-, m,p-, and p,p-quaterphenyls. Table I lists the mole fraction polyphenyl yields based upon

$$\sum_3 Y\phi_3 + \sum_6 Y\phi_4 = 1.00 \quad (1)$$

where $\sum_3 Y\phi_3$ and $\sum_6 Y\phi_4$ are the relative terphenyl and quaterphenyl

yields excluding any biphenyl product derived from the radiolysis of benzene. The basic radiolytic reactions appear to be

where ϕ_1 is benzene, ϕ_2 is biphenyl and the starred species are the radicals, ions, or activated species which were produced by the electron radiation.

The mechanism described by equation (2) shows the overall picture of activated species or radical formation and suggests a scavenging reaction which ultimately leads to the final products. Since radicals must eventually react with radicals, a detailed mechanism similar to the one described by Morrison et al for free radical aromatic substitution is believed to apply here [5]. Morrison et al demonstrated that side reactions (with oxygen, for

TABLE I
MOLE FRACTION YIELDS OF TERPHENYLS AND
QUATERPHENYLS FROM THE IRRADIATION OF BIPHENYL-BENZENE MIXTURES

Product	29.8 Mole % Benzene	49.9 Mole % Benzene	66.4 Mole % Benzene	50.1 Mole % Perdeutero benzene
o- ϕ_3	0.126	0.202	0.244	0.136
m- ϕ_3	0.124	0.195	0.235	0.156
p- ϕ_3	0.113	0.181	0.234	0.126
o,o- ϕ_4	0.050	0.030	0.022	0.050
m,m- ϕ_4	0.084	0.058	0.037	0.075
p,p- ϕ_4	0.051	0.036	0.026	0.047
o,m- ϕ_4	0.175	0.116	0.070	0.158
o,p- ϕ_4	0.118	0.080	0.062	0.114
m,p- ϕ_4	0.158	0.103	0.070	0.137

example) had no significant effect upon isomer distribution and relative reactivities measured by product analysis. In this work no apparent difference was noted between the product distributions of freshly irradiated samples and those which were in contact with air for extended periods.

In free radical aromatic substitution only the relative positional reactivities are measured. In this research the positional reactivities are measured for both the generation of reactive species and the aromatic substitution or scavenging reaction. A general mathematical treatment of this twofold problem may be derived as follows: Let n be the mole fraction of reactive species generated from benzene. Then $(1-n)$ would be the mole fraction of reactive biphenyl species (o-, m-, and p- ϕ_2^*). Specifically, $(1-n)$ is the sum of the o-, m-, and p- ϕ_2^* mole fractions which will be designated as a , b , and c , respectively. Thus:

$$n + a + b + c = 1.00 \quad (3)$$

Any given reactive species (radical or ion) may react with either benzene or biphenyl to produce the polyphenyl products. Let N be the probability that a given radical will react with benzene. Then $1-N$ is the probability that the same radical would react with biphenyl. If the radical reacts with biphenyl, it may do so at three different positions. The scavenging or reactive probabilities of the o-, m-, and p-biphenyl positions are designated as A , B , and C , respectively, such that

$$N + A + B + C = 1.00 \quad (4)$$

From equation (2) and the above definitions, the o-terphenyl yields should be equal to

$$\frac{Y(o-\phi_3)}{Z} = aN + nA \quad (5)$$

where Z is a correction factor because the o-terphenyl yield is based upon equation (1) which does not consider the unknown biphenyl product yield. Similarly, the other product yields may be related to radical formation and scavenging probabilities by

$$\frac{Y(m-\phi_3)}{Z} = bN + nB \quad (6)$$

$$\frac{Y(p-\phi_3)}{Z} = cN + nC \quad (7)$$

$$\frac{Y(o, o-\phi_4)}{Z} = aA \quad (8)$$

$$\frac{Y(m, m-\phi_4)}{Z} = bB \quad (9)$$

$$\frac{Y(p, p-\phi_4)}{Z} = cC \quad (10)$$

$$\frac{Y(o, m-\phi_4)}{Z} = (aB + bA) \quad (11)$$

$$\frac{Y(o, p-\phi_4)}{Z} = (aC + cA) \quad (12)$$

$$\frac{Y(m, p-\phi_4)}{Z} = (bC + cB) \quad (13)$$

The unknown biphenyl yield may be calculated from

$$Y(\phi_2) = \frac{Z-1}{Z} = nN \quad (14)$$

Equations (3) through (14) inclusive provide 12 equations which contain nine unknowns (a, b, c, n, A, B, C, N, and Z). Nine of the equations are independent equations. A program was developed for use on the IBM 7090 Digital Computer for the solution of the above simultaneous nonlinear algebraic equations. Table II lists the results for the nine unknowns.

The radical ratios may be calculated from

$$\frac{\text{Pr}(\phi_2^*)}{\text{Pr}(\phi_1^*)} = \frac{a + b + c}{n} = \frac{1-n}{n} \quad (15)$$

and the scavenging ratios may be calculated from

$$\frac{\text{Pa}(\phi_2)}{\text{Pa}(\phi_1)} = \frac{(A + B + C)}{N} = \frac{1-N}{N} \quad (16)$$

TABLE II

RADICAL AND SCAVENGING PROBABILITIES FOR THE
RADIOLYSIS OF BENZENE-BIPHENYL MIXTURES AT 80°C

Parameters	For Species	29.8 Mole % Benzene	49.9 Mole % Benzene	66.4 Mole % Benzene	50.1 Mole % Perdeutero benzene
a	o- ϕ_2^*	0.142	0.088	0.103	0.172
b	m- ϕ_2^*	0.398	0.275	0.161	0.364
c	p- ϕ_2^*	0.193	0.151	0.098	0.187
n	ϕ_1^*	0.276	0.486	0.638	0.278
A	o- ϕ_3	0.355	0.302	0.213	0.304
B	m- ϕ_3	0.207	0.177	0.170	0.195
C	p- ϕ_3	0.282	0.226	0.210	0.253
N	ϕ_1	0.157	0.295	0.407	0.248
Z	---	1.046	1.167	1.352	1.075
Calculated ϕ_2 Yield		0.044	0.143	0.260	0.070
ϕ_2 Yield from C-14 Analysis		---	0.141 ^[a]	---	---

[a] Average deviation of 0.020.

Some information can be derived from the effect of the initial biphenyl-benzene molar ratios (ϕ_2/ϕ_1) upon these radical and scavenging ratios. Figure 1 shows that a linear relationship exists between the $\text{Pr}\phi_2^*/\text{Pr}\phi_1^*$ and $\text{Pa}\phi_2/\text{Pa}\phi_1$ ratios and the initial biphenyl-benzene molar ratios, ϕ_2/ϕ_1 . These linear relationships can be expressed as

$$\left(\frac{\text{Pr}\phi_2^*}{\text{Pr}\phi_1^*} \right)_x = \left(\frac{\text{Pr}\phi_2^*}{\text{Pr}\phi_1^*} \right)_{1.0} \left(\frac{\phi_2}{\phi_1} \right) \quad (17)$$

$$\left(\frac{\text{Pa}\phi_2}{\text{Pa}\phi_1} \right)_x = \left(\frac{\text{Pa}\phi_2}{\text{Pa}\phi_1} \right)_{1.0} \left(\frac{\phi_2}{\phi_1} \right) \quad (18)$$

where the subscripts x and 1.0 refer to biphenyl-benzene mole ratios of x and 1.0, respectively.

The data in Table II can be used to calculate partial rate factors for radical formation and partial rate factors for scavenging by the various biphenyl positions. The partial rate factors for radical formation may be calculated from

$$r_o = \frac{a}{b} \quad (19)$$

$$r_m = \frac{b}{b} \quad (20)$$

$$r_p = \frac{2c}{b} \quad (21)$$

FIG. 1 RADICAL AND SCAVENGING RATIOS AS A FUNCTION OF ϕ_2/ϕ_1 MOLE RATIOS.

where r_o , r_m , and r_p refer to the partial rate factors for the formation of o - ϕ_2^* , m - ϕ_2^* , and p - ϕ_2^* reactive species, respectively. A factor of two is introduced in equations (21) and (24) to account for the fact that there are half as many para positions as there are meta positions. Similarly, the partial rate factors for scavenging may be calculated from

$$k_o = \frac{A}{B} \quad (22)$$

$$k_m = \frac{B}{B} \quad (23)$$

$$k_p = \frac{2C}{B} \quad (24)$$

where k_o , k_m , and k_p refer to the partial scavenging rates of the ortho, meta, and para positions in biphenyl, respectively. These partial rate factors are listed in Table III. The para position in biphenyl appears to be the best scavenger while the ortho position seems to be the most resistant to radical or ion formation.

The numerical values of k_o and k_p in Table III compare favorably with those of other investigators [1, 2]. In the phenylation of biphenyl ($k_o = 2.1$, $k_p = 2.5$, based on $k_m = 1.0$), Cadogan, Hey, and Williams [2] were working with a single source of radicals, whereas the results in Table III for k_o and k_p are averages for all the radicals, ions, and activated species which were scavenged to give the products noted. Hence, if the reactive species were all radicals, k_p would be the average relative reactivity of the para positions of biphenyl with phenyl, o-biphenylyl, m-biphenylyl and p-biphenylyl radicals. Hutchinson et al [1] obtained average values of 1.8 and 2.5, respectively, for k_o and k_p when biphenylyl radicals (from UV irradiation of 2-, 3-, and 4-iodobiphenyl) reacted with biphenyl; these results compare favorably with their radiolytic k_o and k_p values of 1.5 and 2.9, respectively.

TABLE III
PARTIAL RATE FACTORS FOR THE SCAVENGING AND
RADICAL FORMATION REACTIONS OF BIPHENYL AT 80°C

Mole % Benzene	k_o	k_m	k_p	r_o	r_m	r_p
28.8	1.72	1.00	2.73	0.36	1.00	0.97
49.9	1.71	1.00	2.55	0.32	1.00	1.10
66.4	1.25	1.00	2.47	0.64	1.00	1.22
Average	1.56	1.00	2.58	0.44	1.00	1.10
50.1 ^[a]	1.56	1.00	2.60	0.47	1.00	1.03

[a] Perdeuterobenzene.

The $(Pa\phi_2)/(Pa\phi_1)$ curve in Figure 1 has a slope of 2.5 compared to the predicted slope of 4.0 of Cadogan et al [2]. The large variety of reactive species or radicals (via radiolysis) could well account for this difference. Thus, Cadogan et al predicted that 80 percent of the phenyl radicals would be scavenged by biphenyl in an equal molar mixture of benzene and biphenyl, whereas this radiolytic study indicates that approximately 71 percent of reactive species are scavenged by biphenyl.

The partial rate factor for the generation of o-biphenyl reactive species, r_o , in Table III is significantly smaller than the r_o value of Hutchinson et al [1]. The reason for this difference is unknown; however, in the binary system studied, the small benzene molecules could be exerting a net protective effect on the ortho positions of biphenyl.

By using the ($\text{Pr}\phi_2^*/\text{Pr}\phi_1^*$) 1.0 ratios for benzene and perdeuterobenzene-biphenyl mixtures the isotope effect was calculated to be

$$\left(\frac{\text{Pr}\phi_1^*}{\text{Pr}(\phi_1^*-\text{d}_6)} \right) = \left(\frac{\text{Pr}\phi_1^*}{\text{Pr}\phi_2^*} \right)_{1.0} \times \left(\frac{\text{Pr}\phi_2^*}{\text{Pr}(\phi_1^*-\text{d}_6)} \right)_{1.0} = 2.48 \quad (25)$$

which is in good agreement with predicted ratios for the rupture of C-H and C-D bonds [6].

Carbon-14 benzene was used in the irradiation of an equal molar mixture of benzene and biphenyl to determine the relative biphenyl yield. Excellent agreement (Table II) was obtained between the calculated and experimental biphenyl yields.

In the radiation chemistry of aromatic mixtures the following observations were made. For an equal molar benzene-biphenyl mixture the mole yields of the two radicals were approximately equal. The most important differences were observed in the relative scavenging ratios of the parent molecules. Biphenyl was approximately 2.4 times as effective a scavenger as benzene. From the partial rate factors in Table III, the para positions are the most effective as radical scavengers and the ortho positions in the molecule offer the most resistance to radical formation. An important quantitative bridge exists between radiation chemistry and free radical chemistry.

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