

The Alpha and Gamma Radiolysis of Biphenyl

The application of organic compounds as coolants and/or moderators in nuclear reactors requires that the compound be relatively stable toward ionizing radiations. Radiolytic studies on polyphenyls¹⁻¹⁰ would indicate that, although they are more stable toward ionizing radiations than most organic compounds, they do react at a measurable rate producing polymers (products boiling higher than the parent polyphenyl) as the major product. However, little information has been published about the character of these polymeric products^{3,4,6-8}.

In this work, solid biphenyl (ϕ_2), representing the first member of the homologous series of polyphenyl hydrocarbons, was irradiated with alpha particles from radon and its daughters to study the products formed by the action of heavy ionizing particles on this hydrocarbon. The yields of polymers were determined and their properties were compared with those obtained by gamma-ray radiolysis and by the action of free radicals in solution. The gases evolved during the α -radiolysis were identified.

Resublimed ϕ_2 (mp 71 C, single component by vapor chromatography) was fused on the inside of glass reaction vessels¹¹ and radon was transferred therein. The reaction vessels (RV) were maintained at 25 C except when gases were separated, in situ, cryogenically. After the radon had decayed to tolerance levels the gases were removed and analyzed in a versatile gas-analysis system. The

unreacted biphenyl was removed by distillation under reduced pressure leaving polymers in the RV.

For the gamma radiolysis, biphenyl (88 g) was sealed in an evacuated tube and exposed in a Co^{60} source. Polymer was collected as the residue from the distillation (in vacuo) of the unreacted biphenyl. The gas was not analyzed.

A molten mixture of biphenyl (0.85 mole) and di-*t*-butyl peroxide, a free radical initiator, (0.1 mole) was maintained at 150 C for two hours in a helium atmosphere. The gas formed during the reaction was collected by displacement of water. Vapor chromatography indicated only CH_4 . The residual material in the flask was separated into three fractions by distillation.

The molecular weights of the polymers were determined cryoscopically after dissolving products in benzene or in cyclohexane. Infrared ab-

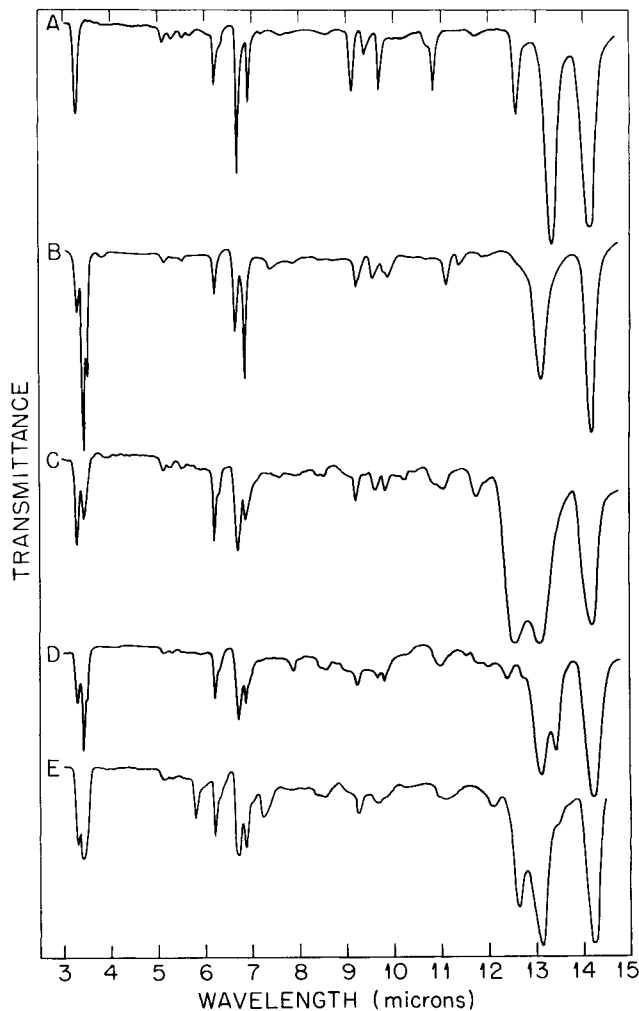


Fig. 1. Infrared absorption spectra of alpha-induced polymer, and related compounds. A, biphenyl; B, phenylcyclohexane; C, alpha polymer; D, gamma polymer, E, FRS polymer.

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TABLE I
Data on Products of Reactions of Biphenyl

Type of Reaction	Energy Absorbed by ϕ_2 ($eV \times 10^{22}$)	Molecules of Gas Produced		Molecules of ϕ_2 Converted to		Molecular Weight ^a of Benzene-Soluble Polymer
		H ₂	CH ₄	Benzene-Insoluble Polymer	Benzene-Soluble Polymer	
Alpha Radiolysis (I)	4.4	1.32×10^{19}	1.21×10^{18}	2.02×10^{19}	1.97×10^{20}	450
Alpha Radiolysis (II)	2.4	1.38×10^{19}	1.85×10^{18}	9.4×10^{18}	1.32×10^{20}	450-500
Gamma Radiolysis	47.0				1.18×10^{21}	390
Free Radicals in Solution						490

^aDetermined cryoscopically in cyclohexane or benzene. The calculated value for biphenyl is 154; for quaterphenyl, 306; and for sexaphenyl 458.

sorption spectra were recorded on an Infra-cord using the viscous polymeric liquids and phenylcyclohexane without solvent. Biphenyl (a crystalline solid) and phenylcyclohexane were examined in solution (CCl₄ and CS₂).

The gaseous products from the radiolysis of biphenyl with alpha particles were about 90% hydrogen and 10% CH₄ (cf., Table I). Different authors^{1,3,4,12} disagree as to the identity of the low molecular weight hydrocarbons that are formed in low yields. It is significant that such hydrocarbons are reported, since it indicates the cleavage of aromatic rings during the radiolysis.

The product that was found in the highest yield (cf., Table I), polymer, was a mixture of materials that boiled higher than biphenyl itself. The polymer was extracted with benzene and the molecular weight determined on the benzene-soluble portion. The benzene-soluble polymer from alpha radiolysis had a slightly higher average molecular weight than the polymer that was obtained in our laboratory by gamma radiolysis. Free radicals in solution (FRS) acted upon biphenyl to produce a polymer that had an average molecular weight similar to that of the polymer from alpha radiolysis.

The yield for the disappearance of ϕ_2 to produce benzene-soluble polymer is about an order of magnitude greater than that to produce the insoluble polymer (cf., Table I). The number of molecules of ϕ_2 going to the benzene-insoluble polymer agrees within a factor of 2 with the number of H₂ molecules produced (cf., Table I). This may indicate that the two polymers are formed by different mechanisms. Possibly the H₂ is evolved in the formation of the insoluble polymer. This hypothesis is supported by the observation that the benzene-soluble polymer is hydrogenated (dis-

cussed below). The benzene-insoluble polymer may be insoluble due to cross-linking and the H₂ may be evolved during this process. These speculations are consistent with the experimental observations and can be expressed as follows:

x biphenyl \rightsquigarrow benzene-soluble polymer (hydrogenated)

y benzene-soluble polymer \rightsquigarrow cross-linked polymer + z H₂.

The average molecular weight (~450) of the benzene-soluble polymer is interpreted to indicate that the most predominant polymer is dimer. This is consistent with previous observations^{4,6}.

The yield (0.50) for disappearance of ϕ_2 to produce benzene-soluble polymer from the α -radiolysis is about twice the yield (0.26) from the γ -radiolysis. This would indicate an LET (linear

TABLE II

Comparison of Yields of Biphenyl Consumed to Produce Polymer

Radiation	Temp.	$G_{(-\phi_2)}^a$	Ref.
1-MeV electrons	100	0.26	10
2.36-MeV protons	100	0.34	13
Pile irradiation (BEPO)	100	0.69	10
α -particles [$B(n, \alpha)$]	100	1.52	10
1-MeV electrons	300	0.38	3
Pile irradiation (BEPO)	300	0.82	3
γ -rays (Co ⁶⁰)	25	0.26 ^b	This work
α -particles (Rn)	25	0.54 ^c	This work

^aThe literature values were reported as G -values. The yields from this work are total yields times 100 (cf., Table I).

^bBenzene-soluble polymer only.

^cAverage value including both polymers.

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energy transfer) effect in solid biphenyl. Burns *et al.*^{3,10,13}, have observed an LET effect in molten biphenyl (cf., Table II) where the $G_{(-\phi_2)}$ for alphas is about six-fold greater than the value for electrons.

Comparative infrared absorption (IR) spectra are shown in Fig. 1 for the benzene-soluble polymer from alpha radiolysis, polymers from gamma radiolysis and from the reaction with free radicals, biphenyl, and phenylcyclohexane. The absorptions due to C-H stretching frequencies in the 3.5 micron region show additional peaks for the other materials that are not present in the biphenyl spectrum. The additional peaks are attributed to the presence of hydrogenated rings in the polymers and in the phenylcyclohexane. The hydrogenation of aromatic rings during the gamma radiolysis of benzene has been demonstrated by Gordon *et al.*¹⁴. Hydrogenation by FRS has likewise been demonstrated by DeTar and Long¹⁵ who isolated dihydro-biphenyl and dihydro-quater-phenyl from the reaction between benzene and benzoyl peroxide.

The polymer from the reaction of FRS contains an absorption peak at 5.8 microns. This is a characteristic absorption region for carbonyl groups and represents the addition of a ketone-

containing fragment to the large molecule. Acetone and its coupling products in reactions of di-*t*-butyl peroxide have been shown to be present by Raley *et al.*¹⁶. Further evidence for the carbonyl group was obtained by the liberation of titratable acid when the polymer was treated with hydroxylamine hydrochloride.

The difference in the spectra of Fig. 1, in the 12 - 15 micron region, have not yet been resolved. The IR spectra of the polymers obtained from biphenyl (Fig. 1) show similarities with those reported by Jones¹⁷ for the polymers obtained by electron radiation of acetylene and benzene.

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