

The Polymerization of Benzene in a Radio-Frequency Discharge

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INTRODUCTION

The reactions of benzene in various types of electrical discharges have been studied by a number of researchers over a span of nearly 70 years. Reported results vary widely. Several early workers (1-3), using ozonizer tubes, obtained a gummy, wax-like substance, along with hydrogen, acetylene and other light hydrocarbon gases. One of these researchers later obtained a liquid and a solid, both analyzing as $C_{24}H_{25}$ compounds (4). In 1930 Austin and Black (5) found diphenyl and a solid which they suspected to be a polyphenylene containing phenol groups. Harkins and Gans (6), using an electrodeless discharge, got complete conversion to a red-brown insoluble solid analyzing for $(CH)_x$. Davis (7), on the other hand, obtained diphenyl, p-terphenyl, a resin $(C_6H_4)_x$, hydrogen, acetylene, ethylene and light paraffins. A 1935 U.S. patent (8) describes a discharge apparatus for preparing diphenyl from benzene. More recently, Streitwieser and Ward (9,10) obtained a 5% conversion of benzene in a microwave discharge, the products being low molecular weight gases, toluene, ethylbenzene and phenylacetylene. Stille and co-workers (11), using a radio-frequency discharge, got a 10% conversion to poly(p-phenylenes); diphenyl, fulvene, acetylene, allene, and methylacetylene. Vastola and Wightman (12) obtained a solid film and concluded from the infrared spectrum of the film that no aromaticity remained in the polymer. Jesch et al (13), on the other hand, also obtained a solid film, but interpreted its infrared spectrum as suggesting the presence of aromatic groups as well as olefinic and acetylenic unsaturation. The wide disparity of the results certainly indicates there is still much to be learned about the chemistry of benzene in electrical discharges. This disparity is probably due largely to widely varying reaction conditions. Especially important are considerations such as the power dissipated in the discharge, the pressure, etc.

The work described here is an attempt to systematize the study of benzene reactions in radio-frequency discharges. The only products isolated in these reactions were diphenyl, a liquid polymer and a solid polymer. The polymers appear to be polystyrenes.

EXPERIMENTAL

Apparatus and Procedure

The apparatus consisted of a 3.69 MHz radio-frequency generator capacitively coupled to a cylindrical pyrex flow reactor by means of two external copper electrodes. An inductively coupled tank circuit was used to match the impedances of the generator and the reactor. An approximate measure of the power dissipated in the discharge was determined by measuring the voltage and current during the experiments and making a phase correction for the capacitive component of the reactor current. A simple schematic of the apparatus is shown in Figure 1.

The hydrocarbon or helium-hydrocarbon mixture was metered into the reactor at various rates. Reactor pressures from 1-20 torr were employed. In most cases the discharge established itself as soon as the r.f. signal was applied. If it did not, it was triggered with a Tesla coil. Products were collected in a series of traps, one at room temperature, one at -78°C and one at -195°C .

Chemicals

Reagent grade, thiophene free benzene (Baker) and vacuum distilled styrene (Matheson, Coleman and Bell) were used in the discharge experiments. The helium (Matheson) had a reported minimum purity of 99.995%.

RESULTS

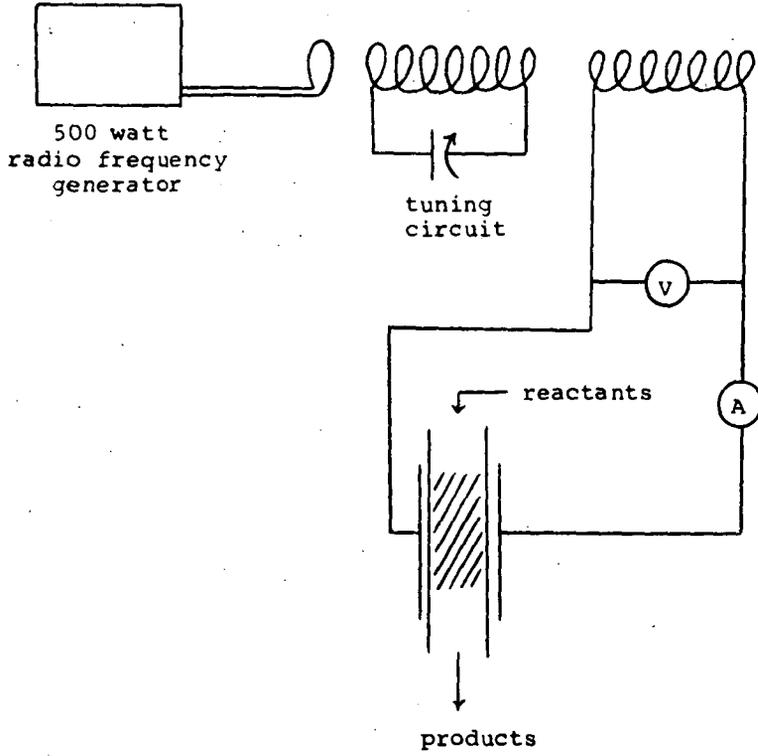
Depending on the conditions employed, the reaction of benzene in the r.f. discharge resulted in either a complete conversion to a solid polymer or a lower conversion to a liquid polymer and diphenyl. The solid tends to form under conditions of high power dissipation and/or low partial pressures of benzene in the reactor. Conversely, the liquid polymer and diphenyl result under low power dissipation and/or high partial pressures of benzene.

The solid polymer, which can sometimes be observed leaving the discharge zone as a fine smoke, deposits throughout the trap system, but principally in the dry ice trap. When collected, it is a very light, fluffy, nearly white powder which picks up a considerable static charge upon handling. Some of the substance's physical and chemical properties are as follows:

1. It is completely insoluble in water and in all organic solvents which were tested.
2. It does not melt up to 435°C .
3. Thermogravimetric analysis shows that the polymer undergoes a stepwise loss in weight, with the loss being complete at 580°C .
4. X-ray diffraction studies show it to be completely amorphous.
5. The density of a pressed pellet is 1.10 g/cc.

Figure 1

Radio Frequency Discharge Reactor



6. A freshly prepared sample was found to have an electron spin density of 2×10^{17} spins/cc.
7. Its surface area (nitrogen adsorption) is $42 \text{ m}^2/\text{g}$, a rather high value for an organic substance.
8. It is neither thermosetting nor thermoplastic.
9. It chemisorbs oxygen from the air at room temperature, the adsorption continuing for extended periods of time.
10. Its carbon-hydrogen ratio is 1:1.

In those experiments which did not yield the solid polymer, the conversion of the benzene was of the order of 30%. About 5% of the benzene was converted to diphenyl; the other 25% was converted to a liquid polymer with an average molecular weight of 617. This polymer, a viscous amber liquid, was not characterized as completely as the solid, but infrared spectral data indicate it to be very similar structurally to the solid.

DISCUSSION

Polymer Structure

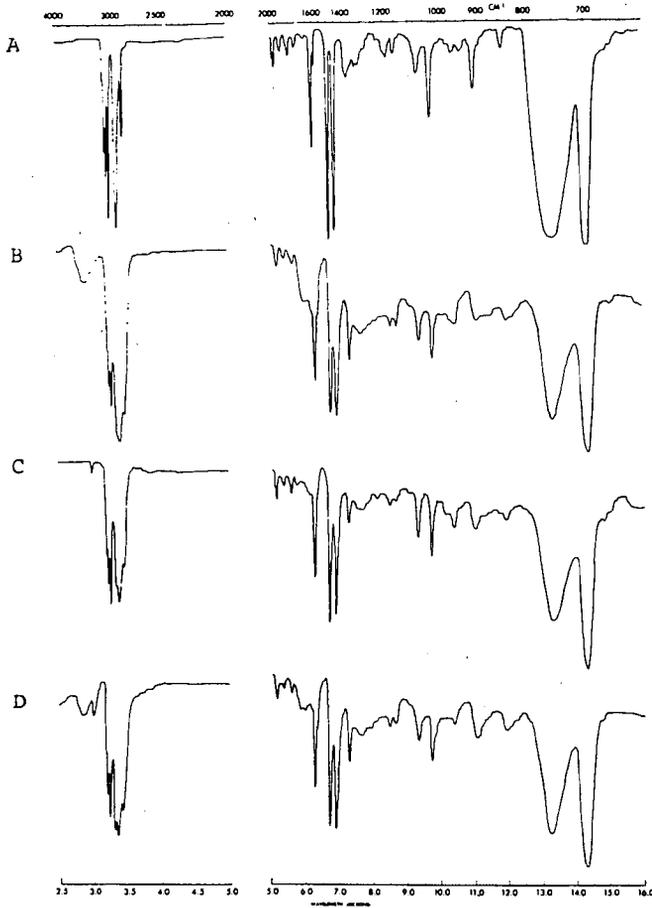
The physical properties of the solid suggest that it is a high molecular weight, highly cross-linked polymer with an irregular structure. The extreme insolubility precludes spectral studies requiring solutions. It was possible to obtain an infrared spectrum by preparing a KBr pellet containing 2% of the solid. The liquid polymer, which was soluble in organic solvents had an infrared spectrum very similar to the solid.

Of several structural possibilities considered, the one which agrees best with the infrared data and seems the most likely from a chemical viewpoint is a polystyrene type structure. In Figure 2, the infrared spectrum of a reference polystyrene film (A) is compared with the spectra of the solid (B), the liquid (C) and a solid polymer obtained when a styrene-helium mixture was passed through the discharge (D). The spectra are nearly identical, the only significant differences being the OH absorptions in the $3300\text{--}3400 \text{ cm}^{-1}$ range and the carbonyl absorptions at about 1700 cm^{-1} . These bands in all three of the spectra from the discharge-derived polymers are due to rapid oxidation by molecular oxygen. These bands become quite pronounced if the polymers are allowed to stand in air for a few hours.

It is believed that the principal difference between the solid and liquid products is that the liquid is essentially a linear polymer, while the solid is highly cross-linked. Such a highly cross-linked polystyrene would be expected to have a lower ratio of aromatic C-H to aliphatic C-H bonds than would a linear polymer. Comparison of spectrum B or D with C in Figure 2 shows that the intensity of the C-H stretching vibrations agrees with this expectation.

Because the solid and liquid seem to be structurally similar, the NMR spectrum of the latter was examined and compared with that of an authentic polystyrene sample. As is generally true with polymeric materials, the resolution was quite poor and only broad bands were

Figure 2. Infrared Spectra

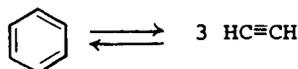


- A = Polystyrene film
 B = Solid polymer from benzene
 C = Liquid polymer from benzene
 D = Solid polymer from styrene

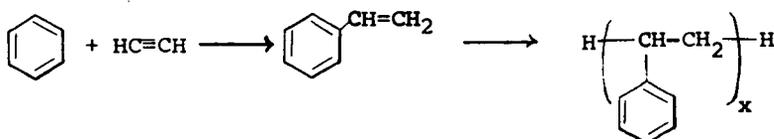
observed. The polystyrene (10% solution in CCl_4) spectrum simply showed two broad peaks - one centered at $\delta = 1.50$ due to aliphatic protons and one at $\delta = 7.08$ (with a small companion peak at $\delta = 6.58$) due to aromatic protons. The spectrum of the liquid polymer (10% solution in CCl_4) was quite similar with the peaks appearing at $\delta = 1.60$ and 7.04 (no peak at $\delta = 6.58$). In addition, a very small peak at $\delta = 5.70$ was observed. This is probably due to protons on olefinic double bonds, and suggests either that some unsaturation is present in the polymer backbone, or that some unpolymerized vinyl groups are present. An attempt was made to increase the resolution of the NMR spectra by using a time averaging computer on very dilute solutions of the polymers, but the resolution was unchanged. Though of limited value, the NMR data do support a polystyrene type structure. Coupled with the infrared data, it seems quite likely that the polymers are both polystyrenes.

Mode of Formation of Polymer

The most likely route from benzene to polystyrene involves several steps, the first of which is the establishment of an equilibrium between benzene and acetylene:

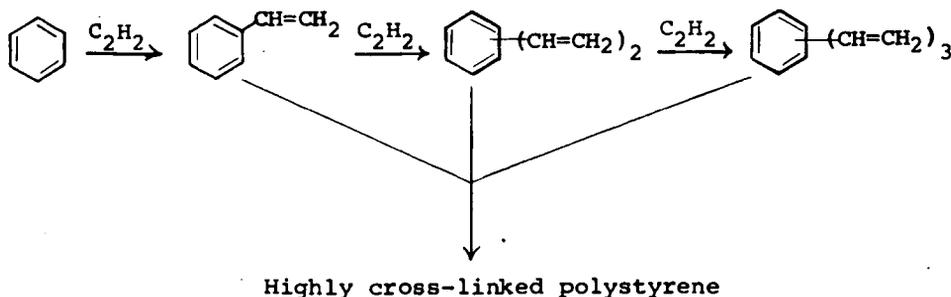


This interconversion has been observed in many high energy systems including electrical discharges. In the next step, the benzene and acetylene, one or both of which may be in a reactive state, combine to give styrene which then polymerizes:



The simple linear polymer thus formed, limited to small chains such as pentamers, hexamers, etc., would explain the liquid polymer product.

The formation of the highly cross-linked solid polymer can be explained by postulating the formation of polyvinylbenzenes which, when polymerized, would yield an extensive, irregular structure:



Both ionic and free radical mechanisms can be written to explain the foregoing reactions in more detail, but these would be strictly speculative, since no definitive experimental evidence has been obtained. Some sort of benzene ions must form as a result of inelastic collisions between the electrons and benzene molecules in the plasma, but whether these ions or some derivative species are the reactive intermediates is not known. Recently, Potter et al (14) have shown that styrene, when perfectly dry, does polymerize via an ionic mechanism when irradiated with gamma rays. One can picture a similar mechanism occurring in the electrical discharge.

On the other hand, the fact that the polymer has a high electron spin density suggests free radical involvement. However, it can be questioned whether the unpaired electrons arose during or after the polymerization reaction. An attempt was made to induce a spin signal in a finely divided polystyrene sample by passing the solid through a helium discharge. No signal was detected after this treatment.

The question of mechanism must await the results of more fundamental studies of the phenomena occurring within the discharge.

Effect of Reaction Variables

In an attempt to find a correlation between the reaction conditions and the type of polymer obtained, about 50 experiments were examined. The dependence of the nature of the product and the benzene conversion on r.f. power dissipated per mole of benzene was tested first. Those experiments which gave a complete conversion to solid polymer had an average dose of 1.9×10^7 watt-sec/mole ϕH . Those which gave a low conversion to liquid polymer plus diphenyl had an average dose of only 7.0×10^6 watt-sec/mole ϕH . This correlation with dose is reasonable since more energy would be required to furnish the additional acetylene required for cross-linking and to gain the complete conversion.

A number of experiments within the group examined were conducted with varying proportions of helium, neon and argon mixed with the benzene. The presence of these gases did not alter the correlation with dose provided that the r.f. power dissipated was considered as deposited in the benzene alone. This is a reasonable presumption because the ionization potential of these gases is well above that of benzene.

Within the group of experiments, some produced solid polymer at doses as low as 4.9×10^6 watt-sec/mole ϕH , but with reduced conversions. This suggests that while the dose does correlate with the conversion obtained, it alone does not determine the product. It is evident that this system will require additional investigation to understand how the products form.

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