The Vapor-Phase Dehydrogenation of Ethylbenzene Using Polymeric & Polymer-Supported Quinones

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Pickard,

Simeon T.

1986
THE VAPOR-PHASE DEHYDROGENATION OF ETHYLBENZENE
USING POLYMERIC AND POLYMER-SUPPORTED QUINONES

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Simeon T. Pickard
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THE VAPOR-PHASE DEHYDROGENATION OF ETHYLBENZENE
USING POLYMERIC AND POLYMER-SUPPORTED QUINONES

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ACKNOWLEDGEMENTS

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Polymer-supported and polymeric quinones were synthesized and evaluated in their ability to dehydrogenate ethylbenzene in the vapor phase. The polymeric quinones were found to be more useful agents for dehydrogenation than the polymer-supported quinones, probably due to the higher concentration of quinone per given mass of polymer.

The factors that affected the yield of styrene using the polymeric quinone were the nature of the polymer, the space velocity in the column, and the reaction temperature. The space velocity was evaluated by holding constant the flow rate of the carrier gas and varying the concentration of ethylbenzene in the gas stream. The best yields were obtained by introducing 0.25 ml of reactant into the column every ten minutes. Using this process the yield of styrene varied from 2.73% at 200°C to 6.90% at 250°C. Both nitrogen and air were used as the carrier gas in this process, and there was no significant difference in the yield of styrene. However, the ability of air to re-oxidize the quinone or its tendency to form undesirable oxidation by-products was not evaluated.
The effect on the ease of vapor-phase dehydrogenation of adding an electron-donating or an electron-withdrawing substituent to ethylbenzene was evaluated. The electron-donating substituent appeared to have little effect upon the dehydrogenation, but the electron-withdrawing substituent had a negative effect.
CHAPTER I
INTRODUCTION

Styrene is an extremely important product of the petrochemical industry, being the monomer for polystyrene and a major component of many copolymers. Styrene production has increased steadily since the 1930’s, and by 1985 production reached 3388 metric tons per year in the United States alone. (1)

Most styrene is made by catalytic dehydrogenation of ethylbenzene to form styrene and hydrogen gas. The dehydrogenation is accomplished at high temperatures to overcome an unfavorable equilibrium. Therefore, the process requires a large energy expenditure, and as energy costs have increased so has the need for a more economical, low-temperature process. One way to achieve that goal is to couple this reaction with a favorable one and create a favorable overall equilibrium at lower temperatures.

Quinones are a class of compounds noted for their ability to act as agents of dehydrogenation, and their reduction could be coupled with the ethylbenzene-to-styrene reaction to create a favorable equilibrium. Quinones are reactive, selective for dehydrogenation, regenerable, and readily available. However, there are some problems associated with using quinones to effect the dehydrogenation of ethylbenzene. The way quinones are normally employed in
dehydrogenation reactions is in solution phase with a reaction time of several hours. The long reaction times are normally unsuitable for an industrial process, and the product styrene will readily polymerize in a hot solution.

For these reasons it was decided to focus on the possibility of using quinones in a gas phase dehydrogenation process. The low melting point or high vapor pressure of most quinones can be overcome by polymerizing the quinone or attaching it to a polymer support. Japanese workers investigated using one unusual polymeric quinone for the vapor phase dehydrogenation of ethylbenzene, but otherwise there has been little or no work done in this area. Hence, this project was to investigate the feasibility of using polymeric and polymer-supported quinones in the gas phase dehydrogenation of ethylbenzene.
Most styrene is manufactured by direct dehydrogenation of ethylbenzene. The reaction, which is highly endothermic, is typically accomplished at temperatures of 600°C or more. Molar conversion of ethylbenzene is a linear function of temperature. However, if the temperature is much above 610°C thermal cracking of the hydrocarbons results. Thus, there is a trade-off between conversion and selectivity at higher temperatures.

\[
\text{Catalyst} \quad \text{CH}_2\text{CH}_3 \quad \xrightarrow{\text{600°C}} \quad \text{CH=CH}_2 + \text{H}_2
\]

In a typical process the ethylbenzene feedstock is preheated to about 520°C and mixed with superheated steam (710°C) at a molar steam-to-hydrocarbon ratio of about 15:1. The steam acts as a source of heat for the reaction and as an inert dilutant. The mixture is introduced into the reactor at about 630°C and about 138 kPa (20 psi) over a fixed bed of catalyst. As the reaction proceeds the mixture cools to about 565°C, at which time it leaves the reactor.
The conversion of ethylbenzene for a single pass is between 40 and 60\%.(3,4) The product mixture can be enriched by separating out the starting material and recycling it. To accomplish enrichment, the mixture is cooled and a free radical inhibitor is added to prevent polymerization. The mixture is finally distilled under vacuum, the ethylbenzene recycled, and the styrene collected. By recycling the starting material an overall yield of about 90\% can be obtained.

The catalyst used for the reaction is the single most important factor in determining both reaction conditions and yield. The catalyst is commonly about 85\% ferric oxide with chromium and potassium oxides added as stabilizers and coke retardants. Catalysts may also contain a variety of other metal oxides, such as zinc and magnesium, and are usually supported on alumina or bauxite.(3,4,5)

Quinones are a highly reactive class of cyclic enones that could conceivably be used to dehydrogenate ethylbenzene. The oldest and best known of these is 1,4-benzoquinone which is also called p-quinone or simply quinone. Quinones form a reversible oxidation-reduction couple with their corresponding hydroquinones. As a result, they make good dehydrogenation agents that can be fairly easily regenerated.

The reactivity of a particular quinone in a dehydrogenation reaction is largely proportional to its reduction potential. The reduction potentials and
structures of several common quinones are given in Table 1. The fusion of a benzene ring in place of one

TABLE 1
Reduction Potentials of Common Quinones

<table>
<thead>
<tr>
<th>Quinone</th>
<th>Reduction Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Benzoquinone</td>
<td>$E_{aq}^o + 0.699$</td>
</tr>
<tr>
<td>p-Naphthoquinone</td>
<td>$E_{aq}^0 + 0.470$</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>$E_{alc}^o + 0.154$</td>
</tr>
<tr>
<td>$\beta$-Naphthoquinone</td>
<td>$E_{aq}^o + 0.555$</td>
</tr>
<tr>
<td>o-Benzoquinone</td>
<td>$E_{aq,30^\circ}^o + 0.792$</td>
</tr>
<tr>
<td>Diphenoquinone</td>
<td>$E_{alc}^o + 0.954$</td>
</tr>
</tbody>
</table>

of the double bonds results in a lower potential and thus a lower reactivity. The fusion of two rings, as in anthraquinone, has an even greater lowering effect. The ortho quinone typically has a higher potential than the corresponding para isomer and therefore tends to be a more powerful dehydrogenation agent.

Adding substituents to a quinone can change the reduction potential in either a positive or negative
direction. Table 2 shows the effect of various substituents on α-naphthoquinone. (6) An electron-withdrawing

**TABLE 2**

Substituent Effect on the Potential of α-Naphthoquinone

<table>
<thead>
<tr>
<th>A</th>
<th>Effect (mV)</th>
<th>A</th>
<th>Effect (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHCH₃</td>
<td>-252</td>
<td>NHCOCH₃</td>
<td>-67</td>
</tr>
<tr>
<td>NH₂</td>
<td>-210</td>
<td>C₆H₅</td>
<td>-32</td>
</tr>
<tr>
<td>N(CH₃)₂</td>
<td>-181</td>
<td>OCOCH₃</td>
<td>-9</td>
</tr>
<tr>
<td>OH</td>
<td>-128</td>
<td>Cl</td>
<td>+24</td>
</tr>
<tr>
<td>OCH₃</td>
<td>-131</td>
<td>SO₂Na</td>
<td>+69</td>
</tr>
<tr>
<td>CH₃</td>
<td>-76</td>
<td>SO₂C₆H₄CH₃</td>
<td>+121</td>
</tr>
</tbody>
</table>

substituent almost always raises the potential of a quinone, and an electron-donating group has an opposite effect. Two of the most important quinone oxidants demonstrate this effect. Chloranil, tetrachloro-1,4-benzoquinone, has a reduction potential of 742mV and 2,3,-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) has a potential of about 1000mV. (7)

Reduction potential is not the only factor that determines the effectiveness of a quinone as a dehydrogenation agent. Geometric configuration of the
quinone relative to the hydrogen donor is also an important consideration. Diphenoquinone, for example, has a higher potential than o-chloranil; but its ability to dehydrogenate tetralin is poorer than that of o-chloranil, probably due in part to geometric factors. As a general rule, comparisons of dehydrogenations with ortho and para quinones show the ortho isomers to be even more effective than one would expect from the differences in the oxidation potentials alone. However, the increased reactivity is not thought to be due to a difference in mechanism, such as a concerted reaction with the ortho quinone and a step reaction for para quinones.

The most important factor that determines the effectiveness of a quinone dehydrogenation reaction is the nature of the substrate itself. A hydrogen donor such as cyclohexadiene is easily dehydrogenated to benzene, whereas cyclohexane is inert toward dehydrogenation by quinones. Table 3 shows the reactivity of various hydrogen donors toward dehydrogenation by DDQ and Chloranil. In general, hydroaromatics are dehydrogenated with much greater ease than "hydroethylenic" compounds (e.g., dibenzyl), and the initial hydrogen abstracted needs to be labile; i.e., on a carbon adjacent to a highly conjugated system.

Before attempting to couple the quinone hydrogenation reaction with the dehydrogenation of ethylbenzene it is important to consider the thermodynamics of the reaction. The thermodynamics of the ethylbenzene-to-styrene reaction
### TABLE 3

Reactivity of Various Hydrogen Donors toward Dehydrogenation by DDQ and Chloranil

<table>
<thead>
<tr>
<th></th>
<th>Tetralin</th>
<th></th>
<th>Acenaphthene</th>
<th></th>
<th>Dibenzyl</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time(hr)</td>
<td>% Dehydrog.</td>
<td>Time(hr)</td>
<td>% Dehydrog.</td>
<td>Time(hr)</td>
<td>% Dehydrog.</td>
</tr>
<tr>
<td>Chloranil*</td>
<td>20</td>
<td>100</td>
<td>20</td>
<td>59</td>
<td>20</td>
<td>&lt;10</td>
</tr>
<tr>
<td>DDQ**</td>
<td>2</td>
<td>100</td>
<td>20</td>
<td>79</td>
<td>20</td>
<td>43</td>
</tr>
</tbody>
</table>

* In boiling xylene, 135°C.
** In boiling benzene, 80°C.
[reaction (1)] reveals the large energy debt that must be supplied for the reaction to proceed. On the other hand, the energetics of the hydrogenation of benzoquinone [reaction (2)] is very favorable. By coupling the two reactions [reaction (3)], the end result is theoretically an exothermic reaction that has a favorable equilibrium.

A second important consideration is the kinetics of the overall reaction and the mechanism by which it would proceed. The kinetics of the solution phase dehydrogenation of dihydronaphthalene using quinones was studied by Braude et al. and the reaction was determined to be basically...
bimolecular and to follow an ionic, two-step mechanism. (10) The mechanism involves the abstraction of a hydride ion from the hydrocarbon by the quinone as the rate-determining step.

\[
\text{(4)} \quad RH_2 + Q \xrightarrow{\text{slow}} R-H^+ + Q-H^- \xrightarrow{\text{fast}} R + QH_2
\]

As would be expected from the mechanism, electron-donating substituents on the hydrocarbon can greatly enhance the dehydrogenation, and electron-withdrawing substituents tend to have an opposite effect. As an example, the addition of \textit{para} methoxy groups to dibenzyl increased the yield of the corresponding stilbene (mostly \textit{trans}) by more than 40%. (7,13) Even so, the reaction took 18 hours to go to completion, which is typical of the dehydrogenation of a hydroethylenic molecule. The reaction of DDQ with ethylbenzene yields no simple dehydrogenation product, which could be due in part to the styrene polymerizing as it is formed.

The vast majority of the work that has been done with quinones has been in the solution phase, and very little has been done with gas phase dehydrogenation. If reaction (3)
were carried out in the vapor phase the mechanism would undoubtedly change from an ionic to a free-radical type. The reaction would still be bimolecular and the abstraction

\[ \text{RH}_2 + Q \xrightarrow{\text{slow}} \text{RH}^+ + \text{QH}^- \xrightarrow{\text{fast}} R + \text{QH}_2 \]

of the initial hydrogen would still most likely be the rate-determining step. However, factors such as the effect of the substituents of the hydrocarbon and the effect of the oxidation potential of the quinone, which are fairly predictable in solution reactions, may well be changed.

Another consideration that arises when the quinone dehydrogenation reaction is carried out in the vapor phase is the physical properties of the quinone itself. Many quinones have rather low melting points, and many others have high vapor pressures at even moderate temperatures (150-200°C) which could make the problem of handling the quinone very difficult. In order to overcome this problem, quinones have been polymerized to be used in vapor phase dehydrogenation reactions.

Japanese workers, Iwasawa et al., made a polyquinone by treating 1,7-naphthalenediol with nitric acid. They obtained a high melting (>300°C) polymeric quinone that was capable of dehydrogenating ethylbenzene vapor in the presence of oxygen. The yields obtained ranged from about
1% at 170°C to 9.1% at 270°C. The oxygen apparently served to reoxidize the quinone because the dehydrogenation still occurred in the absence of oxygen. The yields gradually decreased as the quinone was reduced, but when oxygen was reintroduced into the system the reactivity was regained. Additionally, it was found that small amounts of palladium or ferric chloride enhanced the reactivity of the quinone.

A second way in which a high melting, non-volatile solid can be obtained without polymerizing the quinone is by attaching the quinone to a polymer support. Polymer-supported reactions have become increasingly important in the last several years, and there are a few examples of reactions involving polymer-supported quinones. The polymer-supported quinone can be made via a Friedel-Crafts type reaction between a halomethylated quinone and a polystyrene bead or between a chloromethylated polystyrene bead and a hydroquinone. No examples have been found in the literature of polymer-supported quinones being utilized in the dehydrogenation of a hydrocarbon.
CHAPTER III
EXPERIMENTAL

A. Instrumentation

1. Gas Chromatography

All reaction product analyses were performed using a Varian model 3700 gas chromatograph with a flame ionization detector. The column used was 6 feet long, 1/4 inch O.D., 2 mm I.D. glass, packed with an experimental absorbent: 3% C_{87}H_{6} on Chrom W HP. The data were automatically recorded and integrated by a Hewlett-Packard 3390A integrator and values were used uncorrected. The styrene-ethylbenzene mixtures were readily separated at a column temperature of 60°C with a nitrogen carrier gas pressure of 15 psig. The p-methoxy- and p-nitrostyrenes were separated from their corresponding ethylbenzenes at column temperatures of 120°C and 150°C and carrier gas pressures of 17 psig. and 19 psig., respectively.

2. Infrared Spectrophotometry

Infrared spectrophotometry was used to determine the nature of certain products, especially to evaluate the degree of oxidation of the polymeric quinones. Owing to its sensitivity, a Nicolet MX-10 Fourier Transform infrared spectrophotometer was used. Solid samples were normally analyzed as Nujol mulls since the Nujol did not interfere
with either the carbonyl or the hydroxyl stretching frequencies.

3. Reaction Column

The reaction column was constructed of 61 cm of 5 mm pyrex tubing with two 19/22 ground glass joints attached to each end. Two 300°C thermometers were wired to the column and the column was surrounded by 30 cm diameter pyrex tubing which acted as a jacket. The jacket was wrapped with 24 gauge nichrome insulated resistance wire and connected to a Superior Electric variable autotransformer. A glass wool plug was inserted into the bottom of the 5 mm glass tube to support the polymer material which was added from the top. Diagrams of the apparatus can be found in Appendixes A and B.

4. Other Equipment

A Fischer-Johns melting point apparatus was used to determine melting points. An Ohaus Dial-a-gram beam balance was used to determine most weights. When a more accurate balance was needed a Sartorius analytical balance was used.

B. Syntheses

1. Preparation of Polymer-Supported Quinones

(a) Using plain polystyrene beads. The procedure followed by Blankespoor et al. to make 2-bromomethyl-9,10-anthraquinone was used to prepare 2-bromomethyl-1,4-benzoquinone. Twelve and one-half grams of 2-methyl-1,4-benzoquinone yielded 7 g. of yellow crystals that started to sublime at about 120°C and gave a positive test.
for an alkyl halide. (No value for the melting point was found in the literature.)

Polystyrene beads of an unknown cross-linked density were ground to about the consistency of fine corn meal. Twenty grams of the ground polystyrene, 1.0 g. of aluminum chloride and 1.0 g. of bromomethyl-1,4-benzoquinone were added to 150 ml of heptane and refluxed with stirring for several hours. The resulting product was labeled Polymer I.

(b) Using Merrifield beads. Merrifield beads, chloromethylated polystyrene of 200-400 mesh with 2.63 meq of chlorine per gram and cross-linked with 2% divinylbenzene, were used as a polymer support. Hydroquinone was attached via a Friedel-Crafts alkylation reaction. One gram of ferric chloride, 25.6 g. of Merrifield beads, and 7.4 g. of hydroquinone were added to 150 ml of heptane and the mixture stirred at 25°C for six hours. The resulting beads, Polymer II, were dried under vacuum for several hours and then oxidized with an acidic dichromate solution prepared from 5 g. of sodium dichromate, 5 ml of concentrated sulfuric acid, and 50-75 ml of water.

The product polymers I and II showed no signs of melting at 275°C. However, the infrared spectra of the polymer-supported quinones showed no apparent carbonyl stretch. The absence of the carbonyl in the infrared may have been due to the quinone being localized on the surface of the bead and, therefore, its concentration being too small
with respect to the bead as a whole to show the typical carbonyl stretching absorption.

2. **Preparation of Polymeric Quinones**

(a) Using methylene chloride and hydroquinone. Ten grams of hydroquinone, 6.0 g. of ferric chloride, 500 ml of dried carbon tetrachloride, 60 ml of methylene chloride, and 60 ml of 1,4-dioxane were combined and the mixture refluxed for 24 hours. The product was a black tar that was oxidized with acidic dichromate solution to yield 4.63 g. of Polymer III (M.P. >250°C). The overall yield was 42%. Different Lewis acid catalysts (AlCl₃, BF₃) and slightly different conditions were employed in other preparations, but yields showed little improvement and in some cases actually decreased.

(b) Using methylene chloride and catechol. Four grams of aluminum chloride, 5.0 g. of catechol, 100 ml of carbon tetrachloride, and 50 ml of methylene chloride were stirred at moderate heat for about 2 hours to yield a purple tar. The product was oxidized with acidic dichromate (in acetone) and 4 g. of blue-black polymer, Polymer IV, (M.P. >250°C), were obtained. The yield for the synthesis of Polymer IV (ca. 70%) was typically much better than for Polymer III. However, o-quinone decomposes in water, and thus Polymer IV is more difficult to prepare.

(c) Using phosgene and p-dimethoxybenzene. A polymer from phosgene and p-dimethoxybenzene was attempted via Friedel-Crafts acylation followed by hydrolysis with hydrobromic acid, but the reaction always produced an oil
rather than the desired high-melting solid. Apparently, the second acylation to even a fairly reactive benzene ring proceeds slowly enough that the product is a very low molecular weight polymer. Furthermore, the hydrolysis of the methoxy groups by hydrobromic acid was typically incomplete.

3. Preparation of 4-Ethylanisole

Sixty-eight grams of 4-ethylphenol were neutralized with 20 g. of sodium hydroxide in 50 ml of water and cooled in an ice bath. Sixty-three grams of dimethyl sulfate were added dropwise with stirring and the mixture refluxed gently overnight. The reaction mixture was washed with 50 ml portions of 10% ammonium hydroxide, 5% sodium hydroxide, and water, consecutively. After drying, the product was distilled to give 48 g. of 4-ethylanisole, boiling range 194-6°C. The yield was 64%.

4. Other Chemicals

Other chemicals were either the best grade available in the stockroom or purchased from Aldrich Chemical Company and used without purification with the exception of ethylbenzene, which was purified by fractional distillation.

C. Dehydrogenation Reactions

1. Solution Phase Dehydrogenation using DDQ

The dehydrogenation of ethylbenzene and p-methoxy-ethyl benzene was attempted in solution phase using DDQ. The reaction conditions were those used for the preparation of \textit{trans}-4,4'-dimethoxystilbene. (13)
2. **Vapor Phase Dehydrogenation of Ethylbenzene using DDQ and Chloranil**

Forty milliliters of saturated solution of DDQ in acetone were prepared and 15 g. of 60-80 mesh activated alumina, which had been dried under vacuum at 60°C for 30 minutes, were added. After cooling, the alumina was collected, dried, and placed in the reaction column which was then brought to a constant temperature at 150°C. A plug of glass wool was placed in the top of the column and 2 ml of ethylbenzene were poured onto the glass wool. The carrier gas, which was nitrogen, entered the column above the ethylbenzene and carried it through the column as it vaporized. The same procedure was followed for chloranil. A diagram of the apparatus can be found in Appendix A.

3. **Vapor-Phase Dehydrogenation of Ethylbenzene using Polymer-Supported Quinones**

The reaction column was filled with the quinone-attached polymer beads and ethylbenzene vapor was passed through the column. The process was accomplished by bubbling nitrogen gas through hot ethylbenzene and allowing the gas to carry the ethylbenzene vapor through the column maintained at a temperature of 200°C. The product was collected in a 25 ml round-bottom flask cooled in an ice bath. A diagram of this apparatus can be found in Appendix B.
4. **Vapor-Phase Dehydrogenations using Polymeric Quinones**

The reaction column was filled with polymeric quinone and a plug of glass wool was placed in the top of the column. The sample of material to be dehydrogenated was poured onto the glass wool and the carrier gas introduced into the column above the sample carried the vaporized liquid through the column. The apparatus used in this process is diagrammed in Appendix A.
CHAPTER IV

RESULTS

The purpose of this project was to evaluate the effectiveness of quinones in a vapor-phase dehydrogenation of ethylbenzene. However, it was important to first look at the solution phase dehydrogenation of ethylbenzene as a basis for comparison. As has been noted, the solution phase dehydrogenation of ethylbenzene using DDQ yields no simple dehydrogenation product. However, also noted earlier, the presence of electron-donating substituents can greatly increase the yield in a dehydrogenation reaction. The solution-phase dehydrogenations of ethylbenzene and p-methoxyethylbenzene using DDQ were compared and the results are shown in Table 4. The preparation of trans-4,4'-dimethoxystilbene using DDQ is also shown for comparison. The degree of hydrogenation can be approximated by the amount of 2,3-dichloro-5,6-dicyanohydroquinone formed. The results confirm both the difficulty of the dehydrogenation of ethylbenzene and the positive effect of electron-donating substituents.

Since DDQ and Chloranil are reactive dehydrogenation agents in the solution phase, these quinones were used in a vapor-phase process. There is no simple way of polymerizing DDQ or Chloranil. But, with the boiling point of ethylbenzene being 132.2°C and the vapor pressure of either of
TABLE 4
Results from Solution-Phase Dehydrogenations

<table>
<thead>
<tr>
<th>Starting Material/ Product</th>
<th>Solvent</th>
<th>Temp(°C)</th>
<th>Time(hr)</th>
<th>%Yield</th>
<th>%Hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylbenzene/ Styrene</td>
<td>1,4-dioxane</td>
<td>ca.105</td>
<td>22</td>
<td>0.34</td>
<td>71</td>
</tr>
<tr>
<td>4-methoxyethylbenzene/</td>
<td>&quot;</td>
<td>&quot;</td>
<td>22</td>
<td>16.6</td>
<td>68</td>
</tr>
<tr>
<td>4-methoxystyrene</td>
<td>&quot;</td>
<td>&quot;</td>
<td>22</td>
<td>16.6</td>
<td>68</td>
</tr>
<tr>
<td>4,4'-dimethoxydibenzyl/</td>
<td>&quot;</td>
<td>&quot;</td>
<td>18</td>
<td>83-85</td>
<td>91</td>
</tr>
<tr>
<td>4,4'-dimethoxystilbene</td>
<td>&quot;</td>
<td>&quot;</td>
<td>18</td>
<td>83-85</td>
<td>91</td>
</tr>
</tbody>
</table>

these quinones not excessive below 150° C, it was thought possible to support the quinones on activated alumina and use them in a vapor-phase dehydrogenation. The result was that the alumina-supported quinones turned dark upon heating and there was no apparent reaction with ethylbenzene which passed through the column.

Both Polymers I and II were studied for use in vapor-phase dehydrogenation of ethylbenzene, but Polymer I (plain polystyrene with attached quinone) quickly proved to be less satisfactory than Polymer II (Merrifield beads with attached quinone). As mentioned earlier, the degree of cross-linking of Polymer I was unknown, and apparently the beads absorbed enough ethylbenzene vapor that they began to break down (swell and even fuse) at 200° C. The Merrifield beads reacted in somewhat the same manner, but the process appeared to occur more slowly.
The reaction column was filled with Polymer II, and ethylbenzene vapor was passed through the column. After a tenth of a gram of product was collected, it was analyzed by gas chromatography and found to contain 0.28% styrene. In this same manner, five more samples were collected but the styrene content decreased after the first sample to an average of 0.1%.

The reaction column was then filled with Merrifield beads that had no quinone attached in order to act as a control. The conditions were identical to those of the previous runs, and in the three samples collected the styrene content averaged 0.1%. One explanation for the styrene in the control is that the Merrifield beads contained small amounts of styrene, and the ethylbenzene simply extracted the monomer from the beads. Of course the same process could occur when a quinone is attached. Therefore, when a polystyrene bead is used as a polymer-support in this type of reaction, a few tenths percent styrene in the product is not evidence of dehydrogenation taking place. The low yields of styrene encountered when using the polymer-supported quinone are probably a result of the concentration of the quinone being small with respect to the total mass of the bead.

The polymeric quinones, Polymers III and IV, were tested for their effectiveness in dehydrogenating ethylbenzene in the gas phase. The amount of styrene in the product showed a noticeable increase over the yield of styrene from Polymers I and II (polymer-supported quinones).
The factors that one might expect to effect the yield of
this reaction are the nature of the polymer, the carrier
gas, the space velocity (i.e. the number of moles of
reactant per weight of polymer per hour), and the tempera-
ture. Some of these factors are more easily studied than
others, but all of them were investigated, at least to some
degree, and will be discussed in turn.

Undoubtedly, a very important factor in determining the
yield in this reaction was the nature of the polymer itself.
However, the structure of the polymer (para versus ortho
isomer) seemed to have relatively little effect on the
yield; Polymer III [poly(methylene-p-quinone)] and Polymer
IV [poly(methylene-o-quinone)] gave similar results when
placed in the reaction column. Comparison of the perform-
ance of the two polymeric quinones over a range of tempera-
tures is shown in Table 5. The yields listed are typical,
but there was some variation in yield even for a given
polymer.

The degree of oxidation of the polymer and the particle
size of the polymer seemed to have a greater effect upon its
performance than whether it was Polymer III or Polymer IV.
These two factors are related in that the more finely
divided polymer would be more completely oxidized by the
dichromate solution. However, being finely divided may also
promote dehydrogenation by increasing the surface area of
the polymer and, thus, improving its exposure to the
ethylbenzene. Polymer IVb, which was partially made with
ferric chloride, produces one of the highest yields of
styrene (up to 2.45%) of any of the polymers when using a
Comparison of Performance of Two Polymeric Quinones in Vapor-Phase Dehydrogenation

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp(°C)</th>
<th>Carrier Gas</th>
<th>Feed Vol(ml)</th>
<th>% Styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer III</td>
<td>200</td>
<td>N₂</td>
<td>2</td>
<td>0.85</td>
</tr>
<tr>
<td>Polymer III</td>
<td>225</td>
<td>N₂</td>
<td>2</td>
<td>0.73</td>
</tr>
<tr>
<td>Polymer III</td>
<td>250</td>
<td>N₂</td>
<td>2</td>
<td>0.90</td>
</tr>
<tr>
<td>Polymer IV</td>
<td>200</td>
<td>N₂</td>
<td>2</td>
<td>0.83</td>
</tr>
<tr>
<td>Polymer IV</td>
<td>225</td>
<td>N₂</td>
<td>2</td>
<td>0.71</td>
</tr>
<tr>
<td>Polymer IV</td>
<td>250</td>
<td>N₂</td>
<td>2</td>
<td>0.66</td>
</tr>
</tbody>
</table>
feed volume of 2 ml. Apparently, the ferric chloride had no catalytic effect but the ferric ion may have oxidized the poly-catechol as it formed so that the polymer was more completely oxidized than usual. If this were correct, one would expect the yield of poly-catechol to be low using ferric chloride in the synthesis because the ferric ion could just as easily oxidize the catechol before it had an opportunity to form a polymer and, in fact, the yield was extremely low. In the case of Polymer III, the increased yields of styrene from Polymer IIIb were probably the result of this polymer being more finely divided than Polymer IIIa. These results are summarized in Table 6.

An attempt was made to evaluate the effect of using air instead of nitrogen as the carrier gas in the vapor-phase dehydrogenation reaction using polymeric quinones. The Japanese workers, Iwasawa et al., discovered that when polynaphthoquinone was used in vapor-phase dehydrogenation reactions the carrier gas was critical. When oxygen was used as the carrier gas the quinone was continuously regenerated, but when an inert gas was used the percentage of dehydrogenation soon decreased to virtually nothing. However, the yields using polynaphthoquinone were as great as 9% and the apparatus used by the Japanese workers operated on a continuous flow process. In comparison, the process used in these experiments was a batch-type process and the yields were somewhat lower. Using nitrogen as the carrier gas, a total of 40 ml of ethylbenzene was passed through the column but the polymeric quinone (Polymer IIIb)
<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Temp (°C)</th>
<th>Carrier Gas</th>
<th>Feed Vol (ml)</th>
<th>% Styrene</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-quinone</td>
<td>200</td>
<td>N₂</td>
<td>2</td>
<td>0.83</td>
<td>Polymer IVa - made with AlCl₃</td>
</tr>
<tr>
<td>o-quinone</td>
<td>200</td>
<td>N₂</td>
<td>2</td>
<td>1.23</td>
<td>Polymer IVb - partially made with FeCl₃</td>
</tr>
<tr>
<td>p-quinone</td>
<td>200</td>
<td>N₂</td>
<td>2</td>
<td>0.85</td>
<td>Polymer IIIa</td>
</tr>
<tr>
<td>p-quinone</td>
<td>200</td>
<td>N₂</td>
<td>2</td>
<td>1.3-1.6</td>
<td>Polymer IIIb - same as Polymer IIIa but more finely divided</td>
</tr>
</tbody>
</table>
showed no signs of "fatigue" since yields did not decrease with time. Several runs were made using air as the carrier gas, but as expected there was no appreciable difference in the yields of styrene. When nitrogen was used, the yield of styrene averaged 1.36% versus 1.31% when air was the carrier gas. When air was used as the carrier gas, there was no attempt to analyze for benzoic acid, which is a possible side-reaction product.

One of the most critical factors in determining yield from a reaction of this type is the space velocity in the column. There was no way of directly measuring space velocity with the apparatus that was used. However, the effect of space velocity could be evaluated indirectly by noting the dependence of yield upon the flow rate through the column and the concentration of reactant in the carrier gas stream.

The flow rate through the column was measured by counting the number of drops of product per minute as they came off the column. The performance of Polymer IIIb under a range of flow rates is given in Table 7. The volume of reactant was 2 ml for each run, and the runs are listed in the order they were taken. It is important to note from these data the lack of correlation between flow rate and yield. Therefore, the flow rate may indeed be important but it cannot by itself be a controlling factor in determining yield in the apparatus used.

The concentration of reactant in the gas stream was ultimately the most important factor in determining the
TABLE 7

Effect of Flow Rate on the Yield of Styrene using Polymer IIIb

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Drops/Min</th>
<th>Temp(°C)</th>
<th>% Styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>3.0</td>
<td>200</td>
<td>1.30</td>
</tr>
<tr>
<td>N₂</td>
<td>1.8</td>
<td>200</td>
<td>1.44</td>
</tr>
<tr>
<td>N₂</td>
<td>1.6</td>
<td>200</td>
<td>1.29</td>
</tr>
<tr>
<td>N₂</td>
<td>1.8</td>
<td>200</td>
<td>1.19</td>
</tr>
<tr>
<td>N₂</td>
<td>4.0</td>
<td>200</td>
<td>1.16</td>
</tr>
<tr>
<td>N₂</td>
<td>2.4</td>
<td>200</td>
<td>1.10</td>
</tr>
<tr>
<td>N₂</td>
<td>1.5</td>
<td>200</td>
<td>1.63</td>
</tr>
</tbody>
</table>
yield of styrene from the column. However, since the process was essentially batch-type the concentration of reactant in the gas stream was very difficult to control. Table 8 shows the importance of the reactant concentration on the yield of styrene using Polymer IIIb. It was during the first few and last few drops of product that the yield of styrene was highest. During the middle of the run, when the reactant was flooding the column, the yields dropped off sharply. Varying the feed volume between 0.5 and 2 ml produced little effect on the yield. Apparently, a smaller volume vaporized more quickly and was pushed through the column all at once. However, when the feed volume was decreased to 0.25 ml a significant increase in yield was observed.

The temperature of the column was expected to be an important factor in the yield of styrene because temperature could greatly affect the kinetics of the reaction. Since the concentration of reactant in the gas stream was determined to be so important on the yield, it was necessary to devise an approach so that a change in temperature would have a minimal effect on the reactant concentration in the column. Therefore, only 0.25 ml of ethylbenzene were added at ten-minute intervals; and at higher temperatures (225 and 250°C) the insulation was removed from the top of the column where the feed was added. Removing the insulation slowed the evaporation of ethylbenzene in the neck of the column but did not affect the temperature where the reaction took
TABLE 8

Effect of Reactant Concentration on the Yield of Styrene using Polymer IIIb

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Total Vol (ml)</th>
<th>Sample Size</th>
<th>Temp (°C)</th>
<th>% Styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>2</td>
<td>.5 ml (1st)</td>
<td>200</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.5 ml (2nd)</td>
<td>200</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.5 ml (3rd)</td>
<td>200</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.5 ml (4th)</td>
<td>200</td>
<td>1.47</td>
</tr>
<tr>
<td>air</td>
<td>1</td>
<td>1st drop</td>
<td>200</td>
<td>5.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 ml</td>
<td>200</td>
<td>1.03</td>
</tr>
<tr>
<td>air</td>
<td>1(.25ml/10min)</td>
<td>1 ml</td>
<td>200</td>
<td>2.73</td>
</tr>
</tbody>
</table>
place. The positive effect of temperature increase upon the yield of styrene using Polymer IIIb is shown in Table 9.

Substituted ethylbenzenes were investigated as to the ease with which they would be dehydrogenated in the vapor-phase. In solution-phase dehydrogenations it was seen that electron-donating substituents on the hydrogen donor could greatly enhance the dehydrogenation while electron-withdrawing substituents had an opposite effect. Although the number of runs was insufficient for conclusive results, Table 10 compares the dehydrogenation yields of various ethylbenzenes in the vapor-phase using Polymer IIIb. The presence of the electron-donating p-methoxy group did not have the same positive effect on the dehydrogenation in the vapor-phase as in the solution-phase reaction. However, the electron-withdrawing p-nitro group did appear to have a negative effect in the vapor-phase reaction.
### TABLE 9
Effect of Temperature on the Yield of Styrene using Polymer IIIb

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Feed Vol (ml)</th>
<th>Temp(°C)</th>
<th>% Styrene</th>
<th>% Ethylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>1 (.25/10 min)</td>
<td>200</td>
<td>2.73</td>
<td>97.2</td>
</tr>
<tr>
<td>air</td>
<td>1 (.25/10 min)</td>
<td>200</td>
<td>4.12</td>
<td>95.6</td>
</tr>
<tr>
<td>air</td>
<td>1 (.25/10 min)</td>
<td>200</td>
<td>6.90</td>
<td>92.7</td>
</tr>
</tbody>
</table>

### TABLE 10
Effect of Electron-Donating and Electron-Withdrawing Substituents on the Yield of Styrene

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Carrier Gas</th>
<th>Feed Vol (ml)</th>
<th>Temp(°C)</th>
<th>% Dehydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylbenzene</td>
<td>N₂</td>
<td>2</td>
<td>175</td>
<td>1.09</td>
</tr>
<tr>
<td>4-methoxy-ethylbenzene</td>
<td>N₂</td>
<td>2</td>
<td>200</td>
<td>0.72</td>
</tr>
<tr>
<td>4-nitroethylbenzene</td>
<td>N₂</td>
<td>2</td>
<td>250</td>
<td>0.00</td>
</tr>
</tbody>
</table>
CHAPTER V
SUMMARY

The present industrial process for dehydrogenating ethylbenzene requires temperatures in excess of 500°C. In an attempt to find a suitable low-temperature process (<300°C), polymeric and polymer-supported quinones were investigated as to their utility in a vapor-phase dehydrogenation of ethylbenzene.

Polymer-supported quinones were determined to be less suitable than polymeric quinones because the concentration of quinone was small with respect to the mass of the polymer bead as a whole. Two isomeric types of polymeric quinones were investigated (corresponding to o- and p-benzoquinone) but only small differences in yields of styrene were observed. The yields of styrene using the polymeric quinones varied from 0.85% to 6.9% depending on several factors.

The factors that were determined to effect the efficiency of vapor-phase dehydrogenation using polymeric quinones are as follows: The physical and chemical nature of the polymer, the space velocity through the column, and the temperature of the reaction. The physical and chemical properties of the polymer that were determined to be important were basically the size of the polymer particles and the degree of oxidation. In general, a more finely
divided polymer was more efficient in dehydrogenating ethylbenzene. The space velocity was not easily controlled in the apparatus that was used. However, the highest yields were obtained with a reactant addition rate of 0.25 ml every ten minutes or 1.5 ml per hour. Finally, the temperature of the reaction was critical to determining the degree of dehydrogenation. The highest yield of styrene obtained, which was 6.8%, occurred at a temperature of 250°C. Apparently higher temperatures are needed to overcome the high energy of activation of the reaction.

Future investigations along the lines of this project would most profitably include the following:

(1) Developing an apparatus that will allow the control and measurement of space velocity in a reaction column,

(2) further studies into the effects of using air or oxygen as a carrier gas, to include its ability to re-oxidize the quinone and its tendency to form undesirable oxidation by-products,

(3) further investigations into the effects of temperature upon the reaction,

(4) altering the polymeric quinones to make them more reactive, particularly by adding electron withdrawing groups to the quinone units within the polymer, and

(5) studying the effect of adding small amounts of transition metal salts to the polymer.
APPENDIX A

1. Carrier Gas Flow
2. 5 mm Pyrex Tubing
3. 30 mm Pyrex Tubing
4. Solid Reactant
5. 300°C Thermometer
6. Resistance Wire
1. Carrier Gas Flow
2. Ethylbenzene
3. Heating Mantle
4. Ice Bath


8. Gordon Wilson, Jr., personal communication.


