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Edwin D. Hausmann and C. Judson King

March 29, 1965

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steps involving oxygen are suggested to explain the results, but it is not possible to test any definite reaction mechanism for the oxygen initiated pyrolysis of ethylbenzene reliably.

INTRODUCTION

The thermal decomposition of hydrocarbons is of great interest today. Since the thermal decomposition reaction occurs at relatively high temperatures, many catalysts and other promoters have been investigated with a view towards moderating the reaction conditions and several have been found to affect the reaction significantly. Although thermal decomposition is often carried out as a desirable reaction, there are also situations where thermal decomposition is undesirable such as in nuclear reactor coolants and moderators, and high temperature reboilers. The catalysts now in use to accelerate thermal decomposition reactions are solids such as Cr_2O_3, Al_2O_3, V_2O_5, and Cu, and therefore the reactions involved are heterogeneous.[1,2,3,4] Homogeneous acceleration of the rate of hydrocarbon decomposition has been observed using several substances as additives in low concentrations. Vapors such as azomethane, diacetyl, diethyl ether, chloroform, dichloromethane, bromine, mercury, ethylene oxide, dimethylmercury, and oxygen have been found to have such an acceleration effect.[5-8]

Economically and theoretically oxygen is of greatest interest. Since it is in the air, traces of oxygen will be found in all substances in which thermal decomposition would be undesirable. It is readily available at low cost. An investigation involving oxygen will also yield information concerning the mode of attack of oxygen upon hydrocarbons, thereby elucidating hydrocarbon oxidation, an often studied but not yet completely explained area.

The influence of oxygen on the thermal decomposition of hydrocarbons was noted in 1939 by Rice and Polly when they found that the erratic nature of their results could be corrected if all the oxygen were removed from their experimental system.[9] A review of investigations of oxygen-initiated pyrolysis prior to 1956 has been given by Letort.[10] Most of this work was done on partially oxidized compounds such as acetaldehyde, formaldehyde, acetone, and a number of halogenated

hydrocarbons.[11-14] Letort stated that one part of oxygen in 100,000 doubled the initial decomposition rate of acetaldehyde at 477° C.[15] Niclause and Letort have shown that the pyrolysis threshold of acetaldehyde was lowered from 450° C to 150° C by the addition of one part oxygen in 10,000.[16] Oxygen does not have quite as great an effect in the thermal decomposition of hydrocarbons. Maizus, Markovich and Neiman showed in 1949 that the decomposition of n-butane is sensitized by the addition of small amounts of oxygen.[17] They found that the chain length in the oxygen-sensitized reaction fell off rapidly, from 223 at an oxygen concentration of 0.015% to 3 at a concentration 2.51%, and concluded that oxygen acts as both a sensitizer and an inhibitor. Steacie does not believe that oxygen is the cause of the inhibition.[18]

A detailed study of the reaction of n-butane and oxygen at low oxygen concentrations was reported by Appleby, Avery, Meerbott and Sartor in 1953.[19] With 0.5% oxygen the rate of decomposition increased by a factor of 100. They report that pyrolysis rates may be significantly affected by concentrations of oxygen as low as 0.0001%. In 1957, Engel, Combe, Letort, and Niclause confirmed that trace quantities of oxygen greatly accelerate the initial rate and lower the threshold temperature of the pyrolysis of n-butane.[23] They also found the same effect with propane, isobutane, and neopentane. With propane the pyrolysis threshold temperature was lowered from 562° C without oxygen to 475° C with 0.28% oxygen and 425° C with 1.1% oxygen. They discovered that the accelerating influence is limited to the initial stages of the reaction and they found an appreciable increase in the total conversion to unsaturated hydrocarbons. However, they conclude that the inhibiting effect of the unsaturated products prevents this increase from assuming great importance. At 450° C, they were able to increase the rate of conversion of n-butane in a flow system by 25% by the addition of 2.2% oxygen at several points in the reactor rather than at only one.

Most prevous workers have concluded that oxygen is a homogeneous accelerator; however Poltorak and Voevodskii suggest that oxygen initiation occurs as a surface reaction.[33] They use their results for oxygen

sensitized decomposition to extend a theory of heterogeneous initiation of thermal decomposition reactions.

The thermal decomposition of hydrocarbons in the absence of oxygen is generally well understood. Steacie gives an extensive review on this subject in his book.[18] Rice and Herzfeld have postulated a reaction mechanism involving free-radicals which explains the generally observed first order nature of the reactions and also results in theoretical activation energies which agree well with the experimental values.[22] This mechanism is now known as the Rice-Herzfeld mechanism and is shown in general form below.

$$M_1 \longrightarrow 2 R_1 \qquad (1)$$

$$R_1 + M_1 \longrightarrow R_1H + R_2 \qquad (2)$$

$$R_2 \longrightarrow R_3 + M_2 \qquad (3)$$

$$R_3 + M_1 \longrightarrow R_3H + R_2 \qquad (4)$$

$$R_2 + R_3 \longrightarrow M_3 \qquad (5)$$

$$2R_2 \longrightarrow M_4 \qquad (6)$$

$$2R_3 \longrightarrow M_5 \qquad (7)$$
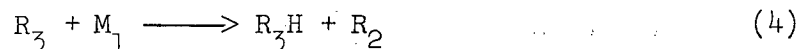
In the first step the hydrocarbon, M_1, dissociates into two radicals, each of which can react with another molecule of hydrocarbon to produce a radical, R_2, which in turn fragments to a product, M_2, and another radical, R_3. This radical continues the chain reaction as shown in step 4. Depending upon which termination reaction—5, 6, or 7—predominates, the reaction order with respect to the hydrocarbon can be 1, 1/2, or 3/2, respectively.

The hydrocarbon chosen for investigation in this work was ethylbenzene. A practical reason for choosing this aromatic hydrocarbon is that aromatic hydrocarbons are the primary constituents of many commercial heat transfer fluids. If small traces of oxygen were found to decrease

the threshold temperature for pyrolysis of these substances significantly, it might be profitable to take meticulous care to exclude oxygen, thereby increasing the temperature range in which these fluids may be utilized. In addition, ethylbenzene was chosen because the stability of the aromatic ring limits the significant thermal decomposition products to benzene, toluene, styrene, hydrogen, methane, ethane, and ethylene at normal pyrolysis temperatures, thereby simplifying the product analysis. Appleby, et al.,[19] reported a marked increase in the yield of olefins with the same carbon number from the pyrolysis of n-butane when oxygen was added. A similar result for ethylbenzene would increase the yield of styrene, and perhaps raise the selectivity for styrene to a level comparable to that given by catalytic dehydrogenation. This is a result which would be of value commercially.

The pyrolysis of ethylbenzene was first investigated by Berthelot, who, in 1869, passed gaseous ethylbenzene through an empty porcelain tube at a moderate red heat.[23] He identified benzene, toluene, styrene, and xylene in the resultant product. A few experiments on the decomposition of ethylbenzene were made by Jost and Muffing in 1941 using a static system.[24] Webb and Corson in 1947, determined the conditions at which the maximum yield of styrene could be obtained by pyrolytic dehydrogenation.[25] A more detailed investigation was conducted by Szwarc in 1949 using a fast flow technique.[26] He reports qualitative results for the pyrolysis of pure ethylbenzene. For more quantitative studies he used toluene as a carrier gas to suppress the reaction chain and obtained dibenzyl and methane as the reaction products. The Arrhenius dependency of the first order rate constant for the formulation of methane he found to be

$$k = 10^{13} \exp(-63,200/RT) \quad .$$

Esteban, Kerr, and Trotman-Dickenson in 1963, also investigated the suppressed chain thermal decomposition of ethylbenzene, this time using an aniline carrier as the radical scavenger.[29] They reported a variation

of the first order rate constant for the formation of methane according to the equation,

$$\log k = (14.6 \pm 0.1) - 70,100 \pm 500)/RT.$$

They state, "although the Arrhenius parameters differ considerably from those found by Szwarc, the rate constants for the middle of the temperature range are the same." This indicates that more work on the thermal decomposition rates of ethylbenzene is justified to clarify the initial decomposition step as well as to examine the full reaction chain.

Recent investigations of the pyrolysis of ethylbenzene have been reported by Lee and Oliver in 1959,[27] and Badger and Spotswood in 1960.[28] The latter study is concerned primarily with trace yields of heavy products.

The only apparent previous study of the partial oxidation of ethylbenzene was carried out at relatively high oxygen concentrations. Jones, et al., employed a raining solids reactor at 415-590° C with a residence time of 5 seconds and an oxygen-ethylbenzene mole ratio of 0.7-1.0.[34] They found that styrene forms essentially all the non-oxygenated aromatic product. For example with 33% conversion of ethylbenzene at 530° C a carbon balance gives a selectivity of 65% to styrene, 15% to benzaldehyde, 8% to acetophenone, 3% to other aromatics and the remainder to gaseous products. With a much lower oxygen content it might be possible to maintain the high selectivity of styrene formation without the simultaneous appearance of oxygenated aromatics which present a separation problem.

With respect to the oxidation of hydrocarbons, an excellent review of gas-phase slow combustion was written by Tipper in 1957,[30] and a review of hydrocarbon oxidation in general was made by Medley and Cooley in 1960.[31] Tipper states that despite the large amount of work already done on slow combustion, the mechanisms of the oxidations are still not altogether clear.

It is generally agreed that the most likely primary initiation step is

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot \qquad (8)$$
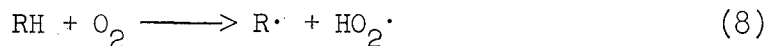
A possible intermediate in the oxidation reactions is a peroxy-radical. Since free radicals are known to combine readily with oxygen it is expected that the reaction

$$R\cdot + O_2 \longrightarrow RO_2^* \qquad (9)$$

will occur creating a peroxy-radical. At the high temperatures of the present studies, it is likely that this radical would decompose to

$$RO_2^* \longrightarrow \text{olefin} + HO_2\cdot \qquad (10)$$
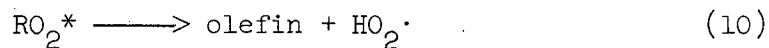
but at lower temperatures it is likely that a chain branching reaction such as

$$RHO_2^* \longrightarrow RO\cdot + OH\cdot \qquad (11)$$

will occur.[31]

It is possible that oxygen or $HO_2\cdot$ takes part in termination reactions, although several researchers have suggested that chain termination is heterogeneous with the reaction occurring at the walls of the reactor.[31] However, by using suitable experimental conditions these surface effects may be minimized. The reactions

$$R\cdot + O_2 \longrightarrow \text{olefin} + HO_2\cdot \qquad (12)$$
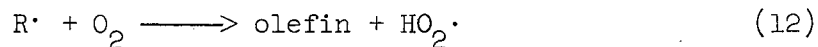
with or without the formation of an intermediate hydroperoxy-radical, and

$$HO_2\cdot + R\cdot \longrightarrow \text{inert products} \qquad (13)$$
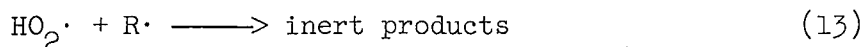
have been suggested as possible termination steps in oxidation reactions.[30] The $HO_2\cdot$ radical is assumed to be unreactive and it is postulated[31] that destruction occurs on a surface by the reaction

$$2HO_2\cdot \longrightarrow H_2O + 3/2\ O_2 \tag{14}$$
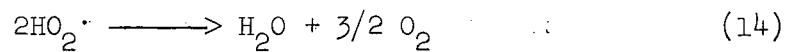
However, it is possible that at higher temperatures the $HO_2\cdot$ radicals begin to propagate the chain by hydrogen abstraction reactions of the form

$$HO_2\cdot + RH \longrightarrow H_2O_2 + R\cdot \tag{15}$$
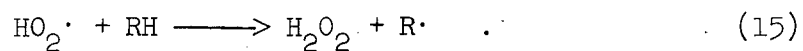
ACQUISITION OF DATA

A. Equipment

The thermal decomposition studies reported in this paper were made using the apparatus shown schematically in Fig. 1. The reactant, ethylbenzene, was vaporized by passing a metered stream of prepurified nitrogen through two sparger-bottles filled with ethylbenzene. These sparger-bottles were partially immersed in a heated oil bath kept at a constant temperature. Adjustment of this temperature allowed achievement of any desired concentration of ethylbenzene in the nitrogen stream. The reactant stream was then preheated in a quartz-chip packed, quartz tube heated by heating tape and two electric tubular furnaces. A metered stream of oxygen then entered via a mixing tee. The thermal decomposition occurred in the quartz reactor which was heated in a pot crucible furnace. After leaving the reactor the product stream was cooled by a cold-water condenser and the condensed liquid product was collected in a flask. The remainder of the condensible products was collected in a trap cooled by a dry-ice-acetone bath in a Dewar flask. The remaining vapors were exhausted to the hood.

The temperatures of the reactant stream were measured in the preheat section and reactor by nine chromel-alumel thermocouples placed at strategic points. Further details of the apparatus and accessory equipment may be found in the appendix.

B. Experimental Procedure

At least 24 hours before a run was to begin the pot crucible furnace was set for the desired temperature and the two tubular furnaces were set slightly below the desired temperature. At least one hour before the run the heating bath was set at the predetermined temperature.
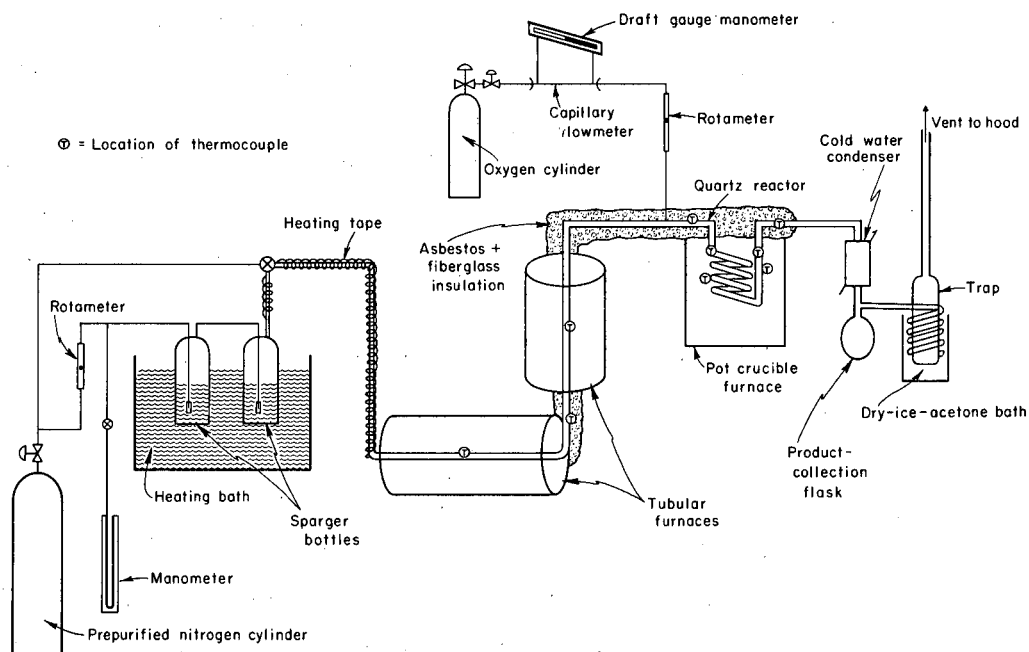
Fig. 1. Schematic diagram of pyrolysis apparatus.

At this time the heating tape was switched on and an oil-pumped nitrogen
stream was passed through the system by-passing the sparger-bottles.
The electric input to the heaters in the preheat section was set at
values which would assure that no pyrolysis occurred before the reac-
tants entered the reactor. One hour after the nitrogen stream was turned
on, it was diverted so that nitrogen would flow through the sparger-
bottles. In 20 minutes steady state temperatures were attained and the
nitrogen was replaced by prepurified nitrogen. After 10 more minutes
the liquid product sample was collected for 10 to 20 minutes depending
upon the flow rates of that particular run. The sparger-bottles were
then refilled with ethylbenzene, and the apparatus was ready for the
next run.

The raw data recorded while the run was in progress included
the input settings of the three furnaces and the heating tapes, the
temperature of the heating bath, nitrogen and oxygen flow meter readings,
the inlet pressure of the system, and readings from the nine thermo-
couples. After the run was completed the liquid product collected was
weighed and a sample injected into the gas chromatograph. The percent-
ages of benzene, toluene, ethylbenzene, and styrene in the product were
calculated from the resulting chromatogram. The readings from the temp-
erature recorders were converted from millivolts to degrees Centigrade
using a conversion table.[*] Oxygen and ethylbenzene concentrations were
calculated from rotameter readings and weight of product collected.

The concentration of ethylbenzene in the nitrogen stream after
passing through the sparger-bottles averaged 65% of the theoretical con-
centration calculated from vapor pressure data. This percentage varied
between 60 and 75% with variation of the nitrogen flow rate through the
sparger-bottles.

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[*]Handbook of Physics and Chemistry, (Chemical Rubber, Co., Cleveland,
Ohio, 1963) p. 2702.

Nitrogen was chosen as the diluent because of its inert character. The reactor and preheat section were constructed of quartz to avoid the possibility of surface effects influencing the reaction. Surface effects should also have been minimized by the high partial pressure (> 1 atm.) of the nitrogen diluent.

The final preheat temperature, as has been mentioned, was predetermined for each flow rate so that a measurable amount of pyrolysis did not occur in the preheat section. For a flow rate of 600 cc/sec this temperature was 440° C, while for a lower flow rate such as 300 cc/sec the maximum preheat temperature was 400° C.

The maximum pressure in the system occurred immediately prior to the sparger-bottles. This pressure varied linearly with the nitrogen flow rate from 960 mm Hg at a flow rate of 12,000 cc/min to 860 mm at a flow rate of 6,000 cc/min.

C.   Experimental Program

The experimental program involved first the determination of the kinetics of the thermal decomposition of ethylbenzene in the absence of oxygen. A set of pyrolysis data was obtained by holding the nitrogen flow rate and furnace temperatures constant and varying the concentration of ethylbenzene. Each time the furnace temperature or nitrogen flow rate was changed a new set of data was obtained in the previously described manner.

After 18 runs which were believed to be reliable and as precise as possible were made and the data analysed, runs were made using small quantities of oxygen for a determination of the magnitude of the effect of oxygen on the thermal decomposition. The data from these runs were evaluated and it was then decided to make several runs at constant residence time, reactor temperature, and ethylbenzene concentration while the oxygen concentration was varied from zero upward. The oxygen-ethylbenzene mole ratio was held below 0.10 to avoid the formation of oxygenated products.

In all, 25 runs with varying oxygen concentrations and 21 runs without oxygen were made.

D. Evaluation and Treatment of Raw Data

The raw data which were obtained consisted of the following parameters: nitrogen, oxygen, and ethylbenzene concentrations and flow rates; nine temperature readings; and the percentages of benzene, toluene, ethylbenzene, and styrene in the product. From these parameters the average or "isokinetic" temperature of the reactor, the residence time, and the rate of formation of styrene were calculated. (The details of these and other calculations may be found in the Appendix.) For the straight or oxygenless pyrolysis these derived data were then fit to an equation of the form of the law of mass action,

$$\text{rate} = A \exp(-E/RT)(EB)^n \qquad (16)$$

where the rate is the rate of formation of styrene, A is the frequency factor, E is the apparent activation energy, R is the gas constant, T is the absolute temperature, EB is the concentration of ethylbenzene, and n is the order of the reaction with respect to ethylbenzene.

This "fitting" was accomplished with a stepwise linear multiple regression code using the IBM 7094 digital computer. In order to perform a multiple regression analysis on the data, Eq. (16) must be transformed by taking natural logarithms, resulting in

$$\ln(\text{rate}) = \ln(A) - E/RT + n \ln(EB) \qquad (17)$$

For the multiple regression $1/RT$ and $\ln(EB)$ were taken as the independent variables and $\ln(\text{rate})$ as the dependent variable. The computer was then used to determine the values of $\ln(A)$, E, and n which best fit a least squares multiple regression on Eq. (17). Similar multiple regressions were made on the data derived from the pyrolysis runs using oxygen.

RESULTS AND DISCUSSION

A. Pyrolysis in the Absence of Oxygen

Reliable data for the rate of pyrolysis of ethylbenzene in the absence of oxygen were obtained from 21 runs. These data are recorded in Table C.1 of the appendix. The data cover a temperature range from $590°$ to $650°$ C, with a three-fold variation of ethylbenzene concentration, and residence times of between 0.07 and 0.18 seconds. The concentration of ethylbenzene was held below 10% in the reactant stream and the reaction conditions were chosen to attain less than 10% total conversion in order to avoid possible secondary reactions such as the formation of polystyrene. The minimum conversion used was 0.50% because of the difficulties in accurate analysis of smaller concentrations.

As expected, the chromatographic analysis of the liquid collected showed that the liquid pyrolysis products consisted of styrene, benzene, and toluene. The distribution of these products and the calculated standard deviations were as follows:

	Selectivity
Styrene	74 ± 3 mole %
Benzene	23 ± 3
Toluene	3 ± 1

This yield pattern showed no apparent trend with respect to reaction temperature or ethylbenzene concentration. Szwarc[26] found these products in the proportions 100:30-40:10-5 when the reaction chain was not suppressed.

A qualitative analysis of the gaseous pyrolysis products was made using the gas chromatograph. Hydrogen was found to be present in the highest concentration. Methane was definitely identified, and ethane and ethylene were tentatively identified as products of the pyrolysis. Approximately 10 times as much ethylene as ethane was produced.

Exact quantitative analyses of the gaseous products were not made because of the low concentrations caused by the large amount of nitrogen diluent. Webb and Carson[25] found approximately equal yields of ethylene and parafinnic hydrocarbons; however they employed much higher conversion levels where secondary reactions would be more important.

The data were fit to a "law of mass action" type equation of the form,

$$\text{Rate of conversion to styrene} = A \exp(-E/RT)(EB)^n \qquad (18)$$

with a multiple regression utilizing the IBM 7094 computer, as noted previously. The values of the parameters thus obtained and their estimated errors are,

$$A = 4.04 \times 10^{12} \ (\text{sec})^{-1} \ (\text{mole/cc})^{0.59}$$
$$E = 68,600 \pm 3,700 \ \text{cal/gm-mole}$$
$$n = 0.41 \pm 0.12$$

The standard error of the resulting correlation is 23%. The validity of these parameters is illustrated by Figs. 2 and 3.

Figure 2 is a typical Arrhenius plot of the logarathm of the 1/2 order rate constant, calculated from the equation

$$k = \text{rate}/(EB)^{1/2} \ , \qquad (19)$$

plotted against the inverse of the absolute temperature. As can be seen the slope of this line is 35° K, which corresponds to an apparent activation energy, E, of 70,000 cal/gm-mole and a frequency factor, A, of $3 \times 10^{13} \ (\text{gm-mole/cc})^{1/2} \ (\text{sec})^{-1}$. The scatter of the data, which becomes more pronounced at the lower temperatures (higher 1/T), is due in part to the low conversion of the reactant which caused the product analysis to be less precise. The data used to plot Fig. 2 are recorded in
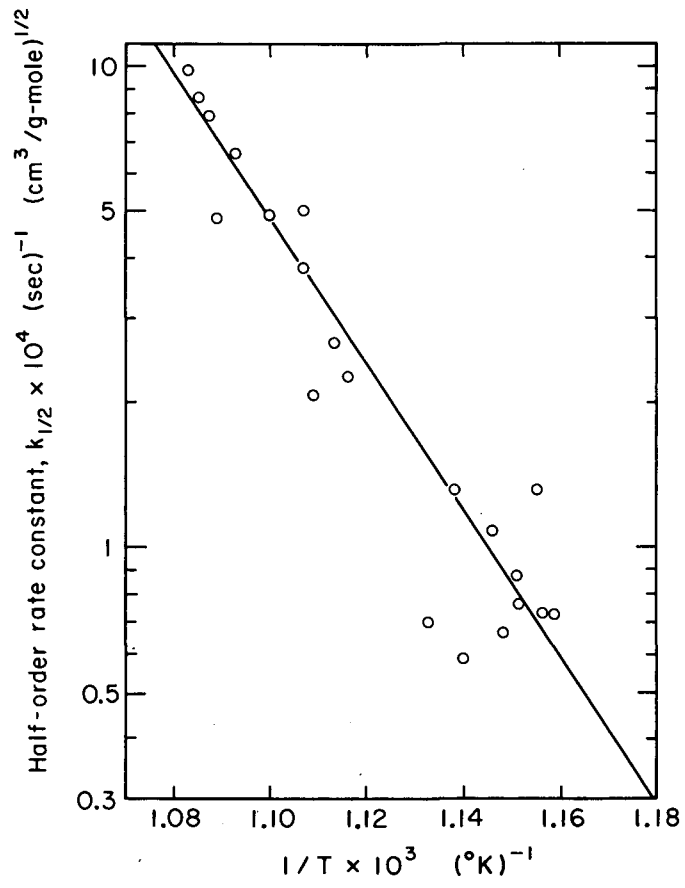
Fig. 2. Arrhenius plot for pyrolysis in the absence of oxygen.
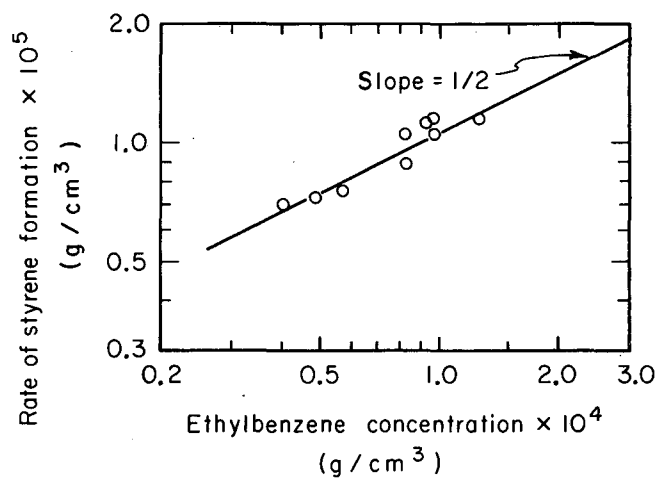
Fig. 3. Determination of order of reaction (the rate of styrene formation is corrected to 600° C).

Tables I and C.1. It is interesting to note that runs with higher and lower than average residence times deviate the most from the line in Fig. 2. This is probably due to changes in the prevalent mechanism of the reaction. For example at higher residence times effects caused by product inhibition, surface reaction, and polystyrene formation would be accentuated. Equilibrium is not a factor since these runs were made so that the conversion was far from that which would be produced at equilibrium.

Figure 3 is a plot of the logarithm of the corrected rate of styrene formation vs. the log of ethylbenzene concentration. Since no more than two runs without oxygen had the same isokinetic temperature, it was necessary to correct the rates of formation of ethylbenzene to a given temperature of 600° C. This was accomplished by choosing the nine runs made at temperatures closest to 600° C and correcting the rates using the equation,

$$\text{rate(at } 600^\circ \text{ C)} = \text{rate(at T)} \cdot \exp[35(1/\text{T}-1/873)] \qquad (20)$$

The slope of the best straight line drawn through the points in Fig. 3 is equal to the order of the reaction with respect to ethylbenzene since

$$\log(\text{rate}) = n \log(\text{EB}) + \text{constant} \qquad (21)$$

The data for Fig. 3 may be found in Table II. As can be seen, Fig. 3 substantiates the 1/2 order with respect to ethylbenzene as was determined with the use of the multiple regression analysis.

As was mentioned in the introduction, the thermal decomposition of hydrocarbons has generally been found and assumed to obey first order kinetics. Sometimes the rate data obtained are not clear, however. In reporting the kinetics of the pyrolysis of n-butane, Echols and Pease state, "The data at once made it clear that only in a most approximate sense could the reaction be called first order."[7] Lee and Oliver reported that the conversion to styrene was about first order with respect

Table I.   Data for Arrhenius plot.

Run No.	(EB) $(\frac{\text{gm-mole}}{\text{cc}})$ $\times 10^6$	$(EB)^{\frac{1}{2}}$ $(\frac{\text{gm-mole}}{\text{cc}})^{\frac{1}{2}}$ $\times 10^3$	Rate $(\frac{\text{mole}}{\text{cc sec}})$ $\times 10^7$	$k_{\frac{1}{2}}$ $(\frac{\text{mole}}{\text{cc}})^{\frac{1}{2}} \frac{1}{\text{sec}}$ $\times 10^4$	$1/T$ $(^{\text{o}}K)^{-1}$ $\times 10^3$
62	.381	.617	.672	1.089	1.146
63	.460	.678	.593	.875	1.151
64	.373	.612	2.94	4.803	1.089
65	.543	.737	3.61	4.898	1.100
66	.785	.886	3.36	3.792	1.107
67	1.251	1.119	2.98	2.663	1.113
68	1.090	1.044	6.87	6.580	1.093
69	.982	.992	2.14	2.159	1.116
70	.908	.953	9.31	9.77	1.083
71	1.058	1.028	9.12	8.872	1.085
72	1.237	1.112	8.85	7.959	1.087
73	.852	.923	.614	.665	1.148
75	.778	.882	.641	.727	1.159
76	.886	.931	.680	.730	1.156
78	.624	.790	.551	.697	1.133
79	1.267	1.225	2.53	2.065	1.109
80	1.025	1.011	.593	.587	1.140
92	.468	.684	3.40	4.970	1.107
98	.795	.892	1.168	1.309	1.155
104	1.086	1.043	.790	.757	1.151
109	1.192	1.092	1.459	1.336	1.138

Table II. Determination of order of reaction.

Run	Δ 1/T ($^{\circ}$K)$^{-1}$	$\exp(E/R \cdot \Delta 1/T)$	rate(at 600°C) (mole/cc sec) $\times 10^7$	EB conc. (mole/cc) $\times 10^6$
62	.001	1.036	.696	.405
63	.006	1.234	.732	.488
65	-.045	.208	.750	.576
66	-.038	.265	.890	.833
70	-.062	.114	1.061	.964
75	.014	1.635	1.048	.826
76	.014	1.635	1.112	.919
104	.006	1.234	.975	1.153
109	-.007	.782	1.141	1.266

Δ 1/T = (1/T - 1/873)

to ethylbenzene at lower temperatures ($550°$ C) and approached zero order at higher temperatures ($650°$ C).[27]

  The following reaction mechanism is suggested as a logical one; it is in accord with the observed 1/2 order of the pyrolysis reaction with respect to ethylbenzene and the apparent activation energy of approximately 70,000 cal/gm-mole.

initiation

$$\text{C}_6\text{H}_5\text{-CH}_2\text{CH}_3 \xrightarrow{k_1} \text{C}_6\text{H}_5\text{-CH}_2\cdot + \text{CH}_3\cdot \qquad (22)$$

$$\text{C}_6\text{H}_5\text{-CH}_2\text{CH}_3 + \text{CH}_3\cdot \xrightarrow{k_2} \text{C}_6\text{H}_5\text{-}\overset{\cdot}{\text{C}}\text{HCH}_3 + \text{CH}_4 \qquad (23)$$

propagation

$$\text{C}_6\text{H}_5\text{-}\overset{\cdot}{\text{C}}\text{HCH}_3 \xrightarrow{k_3} \text{C}_6\text{H}_5\text{-CH=CH}_2 + \text{H} \qquad (24)$$

$$\text{H}\cdot + \text{C}_6\text{H}_5\text{-CH}_2\text{CH}_3 \xrightarrow{k_4} \text{C}_6\text{H}_5\text{-}\overset{\cdot}{\text{C}}\text{HCH}_3 + \text{H}_2 \qquad (25)$$

termination

$$\text{C}_6\text{H}_5\text{-}\overset{\cdot}{\text{C}}\text{HCH}_3 + \text{C}_6\text{H}_5\text{-}\overset{\cdot}{\text{C}}\text{HCH}_3 \xrightarrow{k_5} \text{various products} \qquad (26)$$
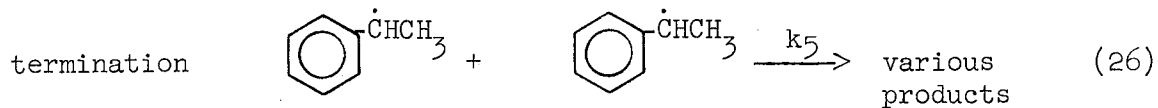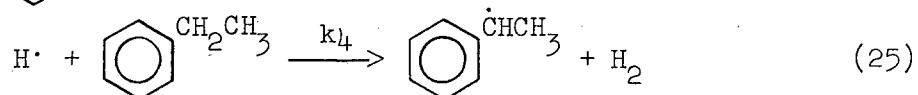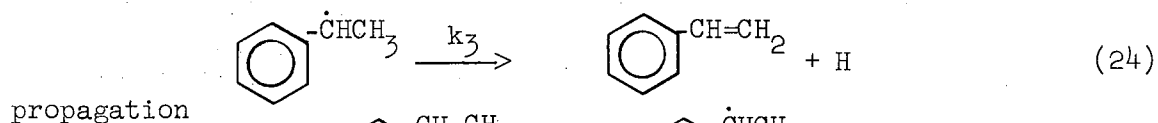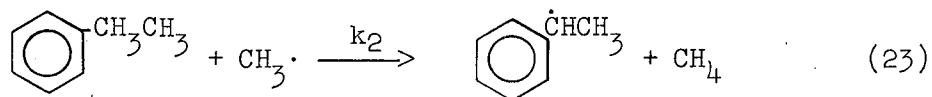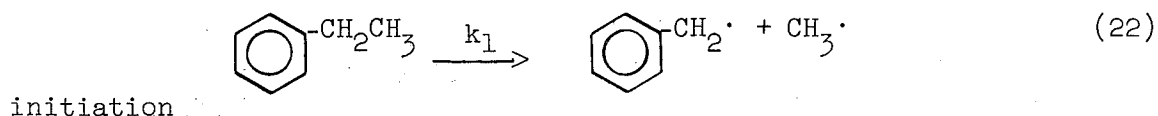
The benzyl radical is known to be unreactive;[26] hence a benzyl radical initiation step similar to reaction 23 has not been included.

  If all the toluene produced is assumed to come from initiation by reaction 22 the yield pattern analysis indicates chain lengths of 25 for the production of styrene. Even higher chain lengths result if toluene is produced also in a propagation reaction. Szwarc reported chain lengths of from 15-25 in the pyrolysis of ethylbenzene without chain suppression.[26] With the long chain assumption, this mechanism results in the following expression for the rate of formation of styrene:

$$\text{rate} = \left[\frac{k_1 k_3^2}{2k_5}\right]^{1/2} (\text{EB})^{1/2} \qquad (27)$$

The termination reaction chosen is logical since a termination involving two hydrogen atoms requires a 3-body collision. The extreme stability of the ethylbenzene radicals provided by the several possible resonance forms afforded by the aromatic ring allows these radicals to accumulate to a larger concentration than any of the other radicals which may be formed in the reaction.

These five reaction steps are not offered as the only reactions which occur during the pyrolysis of ethylbenzene. For example this sequence does not explain the formation of benzene. Benzene may be formed by a variation of the first propagation step such as
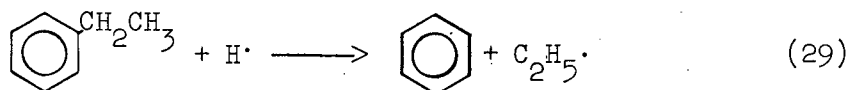
$$\text{(ring)}\overset{\overset{\displaystyle \cdot}{\text{CH}_2\text{CH}_2}}{} \longrightarrow \text{(ring)} \cdot + \text{CH}_2=\text{CH}_2 \qquad (28)$$
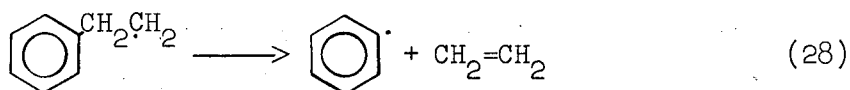
or by a variation of the second propagation step, such as that suggested by Szwarc[26]

$$\text{(ring)}\overset{\text{CH}_2\text{CH}_3}{} + \text{H} \cdot \longrightarrow \text{(ring)} + \text{C}_2\text{H}_5 \cdot \qquad (29)$$

A small amount of toluene may be formed by a modification of reaction 29. A greater yield of e t h y l e n e than ethane was observed, but the ethyl radical from reaction 29 could decompose to ethylene and a hydrogen atom instead of forming ethane through abstraction.

Benzene would be produced in reaction 28 since β-scission occurs if this primary radical is formed and then decomposes. In reaction 24 β-scission cannot occur since no β aliphatic C-C bond is available to break. If the benzene is formed largely by reaction 28 the resulting phenyl radical will probably abstract hydrogen from ethylbenzene by a process similar to reactions 23 and 25:

$$\text{(ring)} \cdot + \text{(ring)}\overset{\text{CH}_2\text{CH}_3}{} \longrightarrow \text{(ring)} + \begin{cases} \text{(ring)}\overset{\overset{\displaystyle \cdot}{\text{CHCH}_3}}{} \\ \text{or} \\ \text{(ring)}\overset{\text{CH}_2\overset{\displaystyle \cdot}{\text{CH}_2}}{} \end{cases} \qquad (30)$$
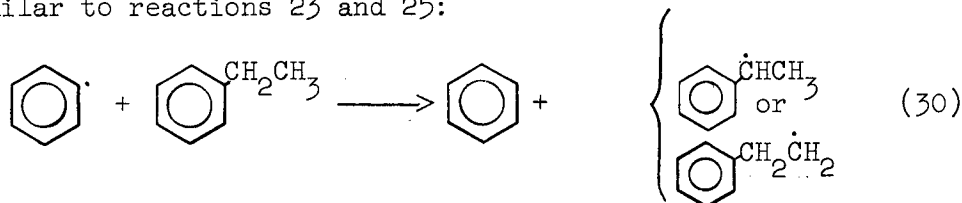
Similarly reactions 23 and 25 could lead to either of the two phenyl-ethyl radicals. If reactions 25 and 30 both produce the same ratio of the two phenylethyl radicals the rate expression for styrene formation, Eq. (27), will be unchanged. Similar reasoning applies if benzene is produced by Eq. (29).

The above mechanism represents a combination of the dominant reaction steps which explains the observed order and activation energy. Approximate values of activation energy and frequency factors as determined from Steacie[18] may be taken for the individual steps in the mechanism. For Eq. (22), $E_1 = 63,000$ cal/gm-mole and $A_1 = 10^{13}$ sec^{-1} from Szwarc's data. For Eq. (24) $E_3 = 40,000$ cal/gm-mole by analogy to similar reactions for other hydrocarbons (ref. 18, p. 509); $A_3 = 10^{13}$ sec^{-1}, assuming a typical unimolecular type reaction. For Eq. (26) $E_5 = 0$ since it is a radical recombination reaction; $A_5 = 10^{14}$ cc/gm-mole sec for a typical bimolecular reaction. Substitution of these quantities into the rate expression, Eq. (27), yields for an apparent activation energy, $E = 71,500$ cal/gm-mole, and for the frequency factor, $A = 2 \times 10^{12}$ (cc/gm-mole)$^{\frac{1}{2}}$(sec)$^{-1}$. This activation energy agrees well with the experimental value of 70,000 cal/gm-mole. The frequency factor is a factor of 10 less than observed but the agreement is adequate if one considers that these steps are not actually molecular reactions, but reaction steps involving free radicals. Also, the assumed values of 10^{13} and 10^{14} are gross approximations which can be modified by steric effects. This mechanism is definitely a form of the Rice-Herzfeld mechanism shown in the Introduction.

B. Oxygen Initiated Pyrolysis

Twenty-five runs with oxygen were made using oxygen-ethylbenzene molar ratios as high as 0.10. No oxygenated hydrocarbons were detected in the analysis of the products from these runs, so it is assumed that the oxygen consumed was converted to water. Appleby, et al., did not observe formation of oxygenated products from n-butane at oxygen concentrations of less than 12%.[19] The data obtained from these 25 runs are tabulated in Table C.2, which may be found in the appendix. Figures 4 and 5 illustrate how small quantities of oxygen increase the rate of pyrolysis, and also how this increase tapers off as the oxygen concentration is increased. The data represented by each curve on these figures were obtained by keeping all variables constant except oxygen concentration, thereby minimizing possible errors. It may be observed from these figures that the temperature for a given conversion level may be lowered about 10° C by adding a small percentage, 3%, of oxygen.

The results obtained in these studies correspond to the results obtained in the investigations of the oxygen initiated pyrolysis of n-butane. The previous work is summarized by Fig. 6 Note that the same type of initial increase in the rate of pyrolysis is found, with a gradual tapering off of this effect. These data were chosen since they represent the same temperature. The data in which a 100-fold increase in the rate of pyrolysis was observed were taken at a much lower temperature.

Not all of the oxygen which was added was consumed in the reaction, for if this were the case an increase in residence time would not result in an appreciable increase in the amount of conversion of ethylbenzene relative to the percentage of oxygen present. As can be seen from Table III, if the residence time is doubled the amount of styrene produced relative to the oxygen concentration is more than doubled. For example compare runs 86 and 99. This table also shows the scatter inherent in the data, but the trend is obvious even with the scatter. This indicates an excess of oxygen in the system which had not yet reacted. In fact

Table III. Effect of residence time on oxygen initiated pyrolysis.

Run no.	Conv. O_2 (cc/sec)	O_2/EB 100 (mole/mole)	$\dfrac{O_2 \text{ Conc.}}{\text{Conv. } O_2}$ (mole/mole)	T_{iso} (^0C)	Res. Time (sec)
86	.17	2.91	7.1	604	0.080
89	.10	3.36	9.9	599	0.083
94	.16	2.71	1.8	630	0.172
99	.13	2.44	3.1	593	0.167
107	.22	1.91	2.9	596	0.118
112	.19	1.93	4.0	605	0.116

Conv. O_2 = Conversion due to oxygen minus that due to straight pyrolysis
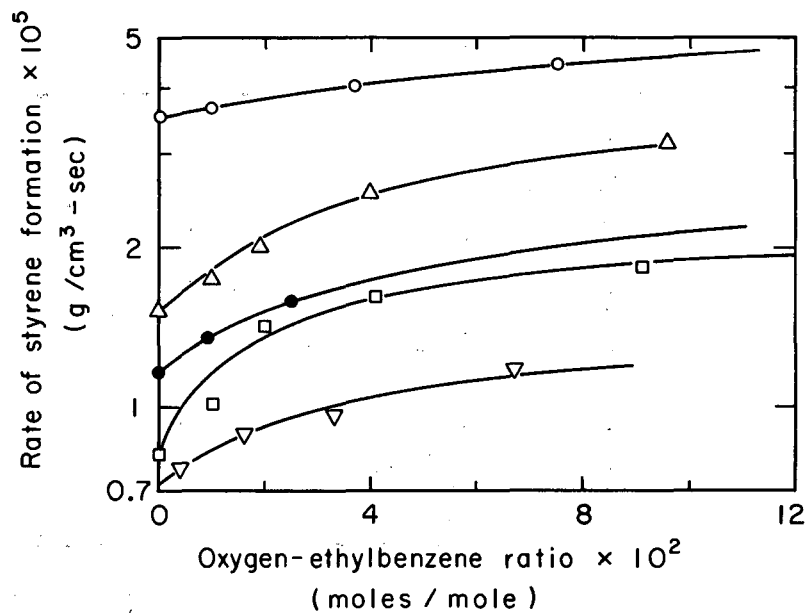
Fig. 4. Effect of oxygen-ethylbenzene ratio on the rate of styrene formation.

	Temp.	Res. Time. (sec)	$(EB) \times 10^4$ (gm/cc)
▽	600°C	0.08	0.7
▣	596°C	0.12	1.1
●	593°C	0.17	0.8
△	605°C	0.12	1.3
☉	630°C	0.17	0.5
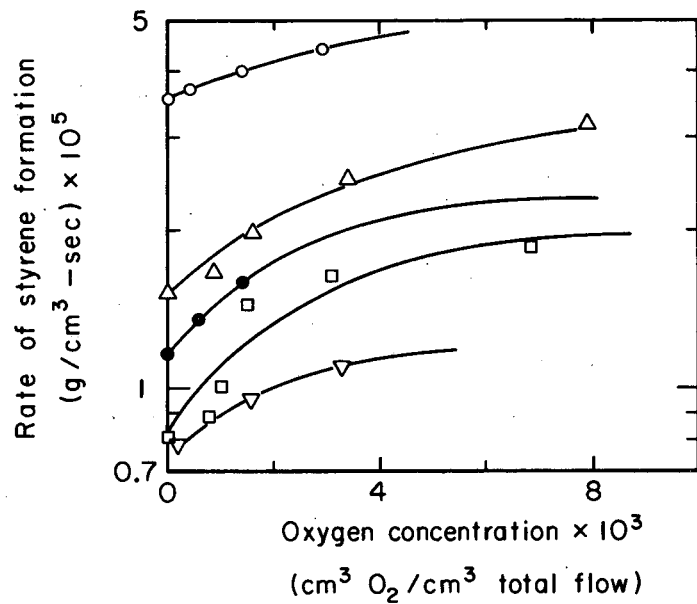
MU-35320

MU-35321

Fig. 5. Effect of oxygen concentration on the rate of styrene
formation.

	Temp.	Res. Time. (sec)	$(EB) \times 10^4$ (gm/cc)
▽	600°C	0.08	0.7
⊡	596°C	0.12	1.1
●	593°C	0.17	0.8
△	605°C	0.12	1.3
⊙	630°C	0.17	0.5
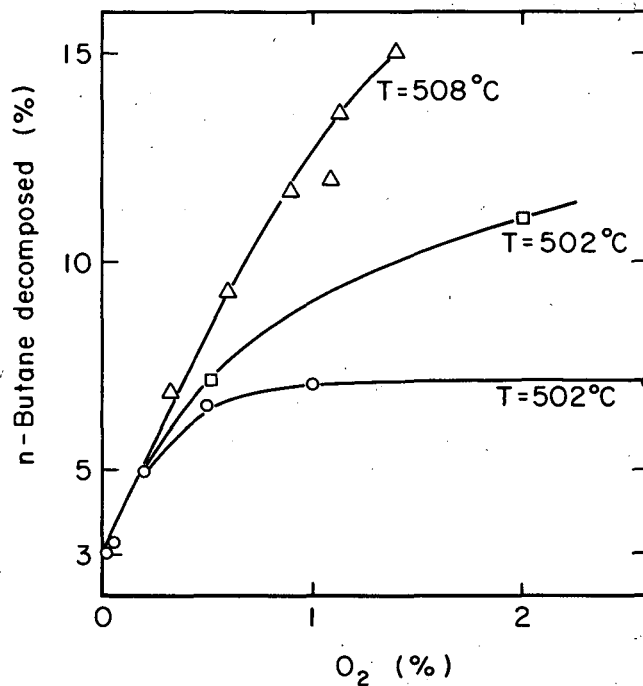
Fig. 6. Oxygen initiated pyrolysis of n-butane.

△ Rice and Polly[9] P_O= 298 mm Hg

▢ Appleby, et al.[19] P_O = 380 mm Hg

⊙ Maizus[17] P_O = 200 mm Hg.

MU-35322

very little of the oxygen which is added is consumed. At a residence time of 0.08 second only 1 mole more styrene is produced for every 5 moles of oxygen added.

The data from the 25 runs using oxygen were fit to a law of mass action type equation,

$$rate = A \exp(-E/RT)(EB)^n (O_2)^m \qquad (31)$$

using a similar multiple regression as that used for the pyrolysis without oxygen data. The data used are tabulated in Table IV. The following values for the parameters were obtained:

$$A = 2.98 \times 10^{11} (sec)^{-1} (moles/cc)^{0.49}$$
$$E = 60,000 \pm 4,500 \ cal/gm\text{-}mole$$
$$n = 0.34 \pm 0.16$$
$$m = 0.17 \pm 0.05 \ .$$

This equation should not be interpreted rigorously, since, at the temperatures used to obtain these data, the rate does not approach zero as the oxygen concentration approaches zero. The above form is suggested only to get a qualitative view of the effect of oxygen. It may be noted that the apparent activation energy decreased from 68,000 cal/gm-mole in the absence of oxygen to 60,000 in the presence of oxygen. This indicates that the oxygen initiated pyrolysis requires less energy to produce a given quantity of styrene. It may also be noted that the reaction order with respect to ethylbenzene decreases slightly from 0.41 to 0.34.

The increase in reaction rate due to the introduction of oxygen was also correlated to another equation of the form of the law of mass action. The data were fit to

$$rate(with \ O_2) - rate(without \ O_2) = A \exp(-E/RT)(EB)^n (O_2)^m \quad (32)$$

Table IV. Data used in regression analysis, runs containing oxygen.

Run no.	T_{iso} (°C)	Rate (gm/cc-sec) $\times 10^5$	EB Conc. (gm/cc) $\times 10^4$	O_2 Conc. (cc/cc) $\times 10^3$
84	624	5.197	.975	3.911
85	624	3.880	.968	1.962
86	604	1.332	.997	1.954
87	604	1.794	.973	3.925
88	599	.970	.719	1.611
89	600	1.270	.715	3.273
90	597	.770	.754	.200
91	597	.889	.761	.814
93	630	4.406	.555	2.911
94	630	4.013	.543	1.409
95	629	3.694	.557	.412
96	607	1.552	.731	.894
97	607	1.378	.715	.410
99	593	1.579	.887	1.368
100	593	1.378	.884	.513
101	638	6.895	1.209	2.393
102	635	5.478	1.228	1.383
105	596	1.847	1.138	6.838
106	596	1.656	1.150	3.075
107	596	1.430	1.129	1.482
108	596	1.015	1.127	.752
110	606	3.142	1.219	7.930
111	606	2.541	1.238	3.420
112	605	1.987	1.250	1.640
113	605	1.646	1.232	.858

by a multiple regression analysis where the rate due to straight pyro-
lysis was calculated from the previous correlation (eq. (18)). The values
of the parameters obtained are

$$A = 7.7 \times 10^9 \ (sec)^{-1} \ (moles/cc)^{0.28}$$
$$E = 48,500 \pm 1,600 \ cal/gm\text{-}mole$$
$$n = 0.02 \pm 0.59$$
$$m = 0.70 \pm 0.18$$

Note the lower activation energy of 48,500 cal/gm-mole which substanti-
ates the previous observation that the activation for the oxygen initiated
portion of the pyrolysis is much lower. Another interesting point is the
zero order with respect to ethylbenzene, although the probable error in
this value is extremely large. The order of 3/4 with respect to oxygen
compares with an order of 1/2 found by Appleby, et al.,[19] for the oxygen
initiated pyrolysis of n-butane.

The application of this type of expression necessitates the
assumption that the pyrolysis due to oxygen occurs independently of that
due to thermal decomposition. It is likely, however, that the thermal
pyrolysis and that due to oxygen share the same propagation chain. It
is likely that the chain initiating reactions include both the thermal
initiation

$$(22)$$

$$(23)$$
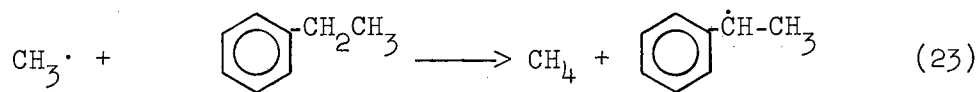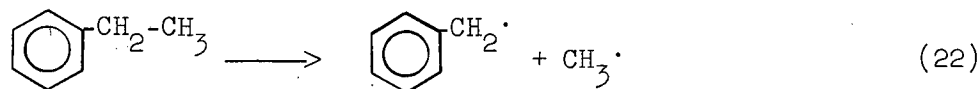
and also an initiation step which includes oxygen, such as

$$(33)$$
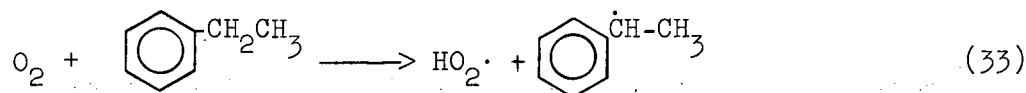
If Eq. (33) is incorporated as another initiation step into the mechanism previously discussed for the formation of styrene the following expression for the rate of formation of styrene results:

$$\text{rate} = \frac{k_3}{(2k_5)^{\frac{1}{2}}} (EB)^{\frac{1}{2}} [k_o(O_2) + k_1]^{\frac{1}{2}} \tag{34}$$

Combining Eqs. (27) and (34) yields

$$\frac{\text{rate with oxygen}}{\text{rate without oxygen}} = [1 + \frac{k_o}{k_1}(O_2)]^{\frac{1}{2}} \tag{35}$$

Figure 7 presents a plot of the square of the rate with oxygen-rate without oxygen ratio vs. the oxygen concentration. Following Eq. (35) this should lead to straight lines with slope k_o/k_1. There is considerable scatter to the data, but straight lines appear to provide a plausible fit at low oxygen concentrations. At higher oxygen concentrations the rate is lower than that predicted by an extrapolation of the low oxygen data.

The form of plotting in Fig. 7 is highly sensitive to errors in the measured rates without oxygen. Figures 8a and 8b present a plot of the square of the rate vs. the oxygen concentration, as suggested by Eq. (34). In this case the relationship is less dependent on the rates in the absence of oxygen. Once again the data appears to fit straight lines at low oxygen levels, but tapers off at the higher oxygen levels.

It is interesting to note in Fig. 7 that the slopes are lower for the higher temperatures. This behavior suggests that k_o/k_1 decreases with increasing temperature, or that reaction 33 has a lower activation energy than reaction 22. The scatter of the data precludes an exact calculation, but to a crude approximation it may be said that the slope in Fig. 7 increases by a factor of 2 every 15-25° C. This figure leads to a difference of 13-21 k-cal/gm-mole between reactions 22 and 33. If E for reaction 22 is 63 k-cal/gm-mole as given by Szwarc,[26] E for reaction 33 is 42-50 k-cal/gm-mole. An activation energy of 40 k-cal/gm-mole
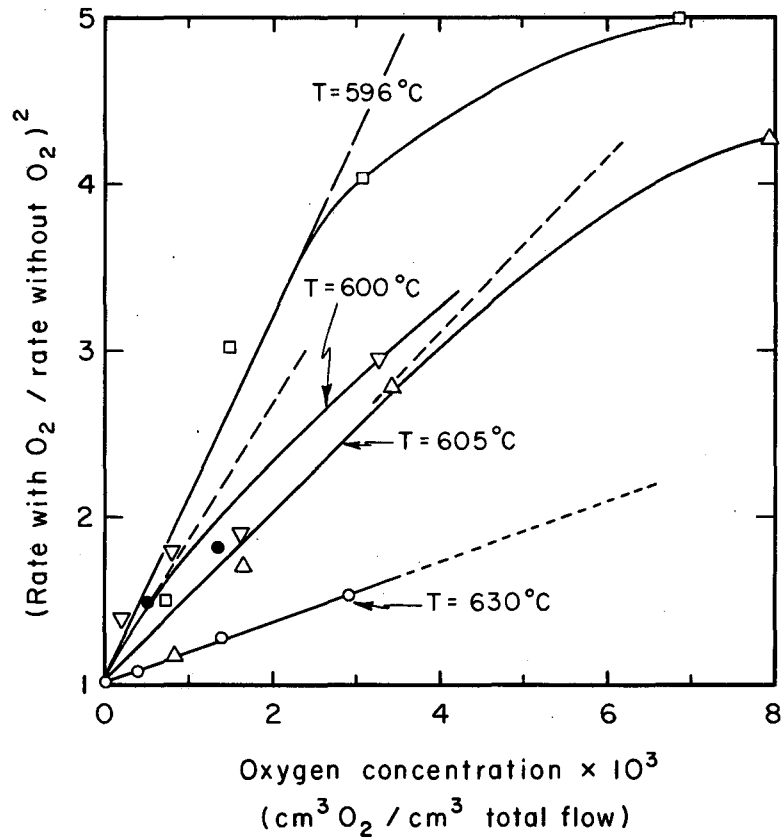
MU-35352

Fig. 7. Increase of rate due to oxygen, according to Eq. (35).

	Temp.	Res. Time (sec)	(EB) × 10^4 (gm/cc)
▽	600°C	0.08	0.7
◻	596°C	0.12	1.1
●	593°C	0.17	0.8
△	605°C	0.12	1.3
⊙	630°C	0.17	0.5
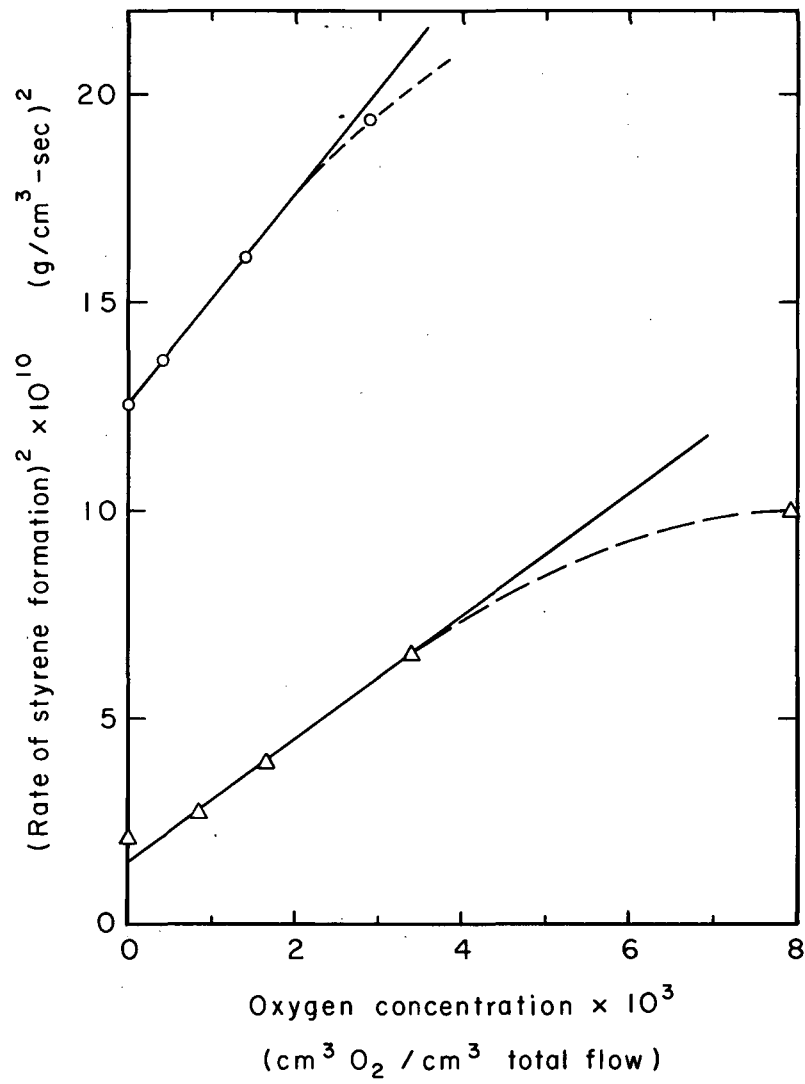
MU-35353

Fig. 8a. Increase of rate due to oxygen, according to Eq. (34).

	Temp.	Res. Time (sec)	$(EB) \times 10^4$ (gm/cc)
△	$605^{\circ}C$	0.12	1.3
⊙	$630^{\circ}C$	0.17	0.5
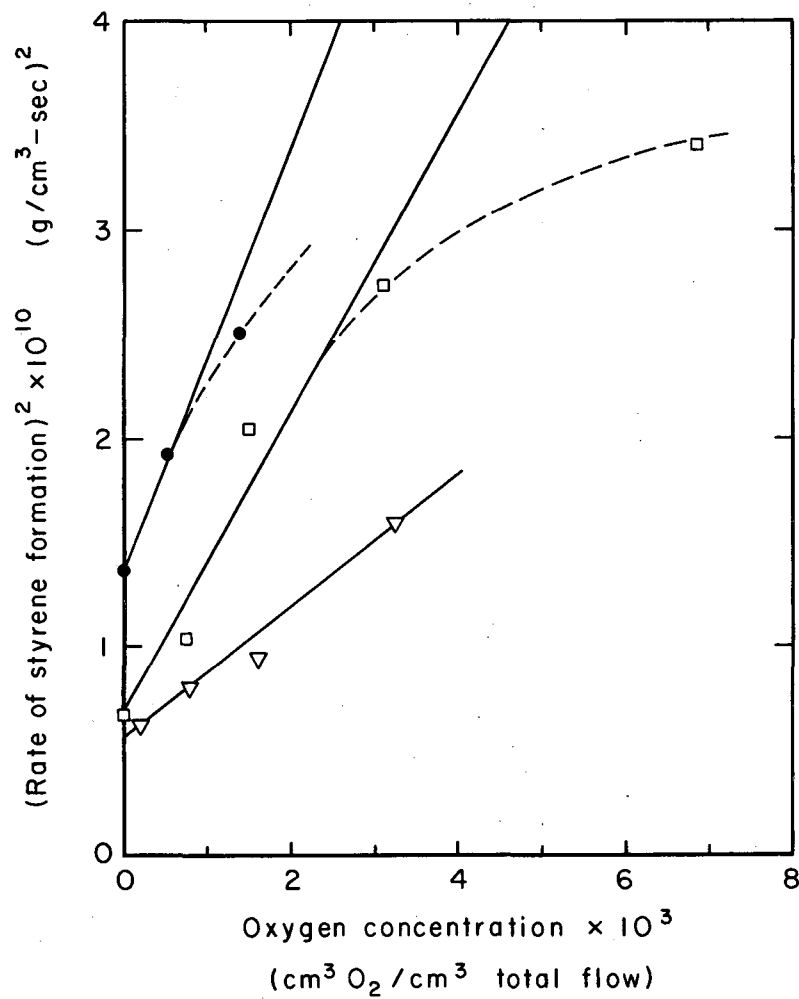
MU-35354

Fig. 8b. Increase of rate due to oxygen, according to Eq. (34).

	Temp.	Res. Time (sec)	(EB) $\times 10^4$ (gm/cc)
▽	600°C	0.08	0.7
▢	596°C	0.12	1.1
●	593°C	0.17	0.8

for oxygen attack of this sort is indicated by Medley and Cooley.[32] An activation energy of 45 k-cal/gm-mole for reaction 33 yields a frequency factor for the same reaction of 3×10^{13} gm-mole/cc sec, which is within the range normally encountered for bimolecular reactions.

The lower activation energy for the oxygen initiation step explains why the effect of oxygen is so much more pronounced at relatively low temperatures for n-butane and suggests a similar behavior for ethylbenzene.

The $HO_2 \cdot$ radical formed is stable enough so that it may not enter into the reaction sequence, but it is possible that the reaction

$$HO_2 \cdot \; + \; \text{[benzene ring]}CH_2CH_3 \longrightarrow H_2O_2 \; + \; \text{[benzene ring]}\dot{C}HCH_3 \qquad (36)$$
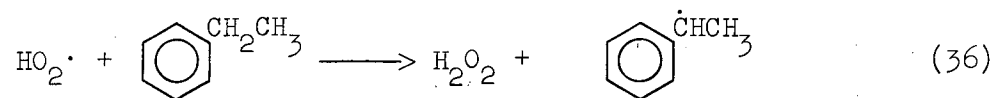
does occur and have a slight effect.

Oxygen may enter the reaction sequence as a chain inhibitor if it reacts like

$$O_2 \; + \; \text{[benzene ring]}\dot{C}HCH_3 \longrightarrow \text{[benzene ring]}\overset{H}{C}=CH_2 \; + \; HO_2 \cdot \qquad (37)$$

or

$$H \cdot \; + \; O_2 \longrightarrow HO_2 \cdot \qquad (38)$$
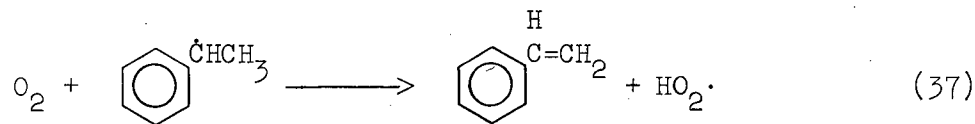
Hydroperoxy-radicals may be formed as intermediates in reaction 37. Initially these reactions would have little effect, but as larger concentrations of oxygen are used these reactions could assume greater importance. Such inhibition reactions may cause the tapering off of the curves in Figs. 7 and 8. Steacie[18] and Engel, et al.,[20] do not believe that oxygen inhibits the reaction, but feel rather that olefinic products cause the inhibition. The results we have obtained do not agree with product inhibition arguments.

As can be seen from Table V, the yield of styrene with respect to the total conversion increases with increasing oxygen concentrations

Table V. Effect of oxygen in the product yield pattern.

Run No.	O_2/EB 100 (moles/mole)	T_{iso} (^oC)	Product distribution (% of total conv.)		
			Styrene	Toluene	Benzene
92	0	630	81	3	16
95	1.0	629	78	3	19
94	3.7	630	81	2	17
93	7.5	630	80	3	17
98	0	593	73	3	24
100	0.9	593	76	2	22
99	2.4	593	76	2	22
104	0	596	72	T	28
108	1.0	596	74	T	26
107	1.9	596	80	T	20
106	4.1	596	81	T	19
105	910	596	81	T	19
109	0	606	72	4	24
113	0.4	505	75	3	22
112	0.7	605	76	3	21
111	1.5	606	80	2	18
110	3.4	606	80	2	18

from about 74% at an oxygen concentration of zero to about 81% at an oxygen concentration of 10% relative to the ethylbenzene concentration. This is the general prevailing trend, since the few points which deviate can be excused as random errors. This increase in styrene yield could result from reaction 37, but it does appear that the styrene yield becomes elevated at oxygen contents below the points where curvature sets in in Figs. 7 and 8. Alternative factors which could give an increased styrene yield include a higher selectivity for benzyl abstraction in reaction 33 than in reaction 25 or a significant contribution of disproportionation reactions as terminations. The chain lengths should decrease as oxygen is increased thereby increasing the styrene yield from disproportionation.

The change in yield pattern confirms the observation of Appleby, et al., that oxygen increases the yield of olefins with same carbon number,[19] although the increase in selectivity is not as striking as found for n-butane.

If reactions 33 and 37 are added to the reaction sequence postulated for the pyrolysis of ethylbenzene in the absence of oxygen, a complex expression for the rate of formation of styrene results. This expression involves a reaction order between zero and one-half with respect to oxygen and between one and one-half with respect to ethylbenzene. Since the rate expression is involved, it would be very difficult to confirm agreement even with more data and more precision among the data obtained.

C. Experimental Observations

These experiments were designed to investigate the initiating effect of oxygen on the pyrolysis of ethylbenzene. Since preceding work using small quantities of oxygen in the pyrolysis of hydrocarbons showed that the effect was limited to the initial stages of the reaction, it was necessary to design an apparatus which could provide a very short

residence time. Therefore a flow apparatus was used. An inherent dif-
ficulty in flow systems with high flow rates is that temperature varia-
tions along the length of the reactor necessitate the calculation of an
average or isokinetic temperature. Such calculations done for this work
are shown in the appendix. Several assumptions necessary for making the
calculations are not rigorously valid; these include the presumption of
plug-flow through the reactor and the neglect of radial temperature
gradients. Since at 600° C the rate of reaction increases 25% for each
5° C rise in temperature, errors in the measurement or calculation of
the reaction temperatures result in appreciable data scatter. We feel
that inaccurate temperatures due to the above causes are the major cause
of the data scatter in this work.

CONCLUSIONS

Oxygen does initiate the thermal decomposition of ethylbenzene, although the effect noted is not as great as that observed for other hydrocarbons such as n-butane. The accelerating effect of oxygen tapers off rapidly so that oxygen cannot be used to accelerate the rate of thermal decomposition of a hydrocarbon more that 100% at very low conversion levels. The decrease in the accelerating effect appears to be due to inhibition of the reaction by oxygen rather than by product inhibition. Oxygen increases the yield of styrene and decreases the yield of benzene but not greatly. It therefore appears that the use of oxygen will not be of especial importance in the commercial production of olefins.

A 1/2 order with respect to ethylbenzene is indicated for the pyrolysis of ethylbenzene in the absence of oxygen. The reaction rates obey the law of mass action with an Arrhenius dependency of the form,

$$\text{rate of formation of styrene} = 4.04 \times 10^{12} \exp(-68,600/RT)(EB)^{0.41}$$

The results agree with those of Lee and Oliver[27] who found an order which varied between zero and one with respect to ethylbenzene and an activation energy of approximately 70,000 cal/gm-mole. The absolute rates are lower than those of Lee and Oliver since they based their temperatures on the maximum reactor temperature rather than the isokinetic temperatures used in this work.

In the evaluation of these results the warning of Steacie should be remembered.[18] "It should be emphasized that, experimentally, complex reactions rarely have orders that are exactly integral or half integral. Further, the order in almost all cases varies with experimental conditions. It is a common fault to attach far too much importance to the exact value of the order of a complex reaction which happens to hold over a narrow range of experimental conditions. Mechanisms derived on such a basis are often grossly oversimplified."

ACKNOWLEDGMENTS

APPENDIX

A. Equipment Details

The apparatus used in this study is shown schematically in Fig. 1. The reactant liquid, ethylbenzene, was vaporized by passing a stream of pre-purified nitrogen, metered by a Fischer-Porter rotameter No. 1420 with floats of stainless steel and glass, through two glass sparger bottles filled with ethylbenzene. The sparger bottles can be taken apart at several O-ring joints for filling and cleaning. These bottles were immersed in a regulated temperature bath filled with Union Carbide UCON lubricant 50-HG-280X. The temperature of the bath was controlled by the combination of a contact thermometer, a mercury-relay switch, and a 1500 watt heater.

The ethylbenzene-vapor-nitrogen mixture then passed through a 3-way stopcock into a 5 ft. long, 12 mm. diameter, quartz-chip packed, quartz preheat section. The preheat section was heated by two sections of electrical heating tape and two tubular furnaces. The electrical input to these heaters was regulated by four Variacs. Insulation for this section of the apparatus was provided by asbestos tape covered by fiberglass.

Oxygen, metered by both a Fischer-Porter rotameter No. 1608 with sapphire and stainless steel floats, and a 2 ft. long, 0.5 mm. diameter, capillary flow meter, entered the reactant stream immediately after the preheat secion and before the reactor. The reaction occurred in the quartz reactor shown in Fig. 9. The reactor was heated in a Lindberg CR-5 pot crucible type laboratory furnace. The reactor was immersed in the air filled pot. The heated air provided a consistent temperature for the entire reactor and sufficient heat transfer for the thermal decomposition reaction.

Immediately after leaving the reactor the product stream was cooled by a cold-water, glass contact surface, condenser and the condensed liquid product was collected in a 250 ml. round bottom flask
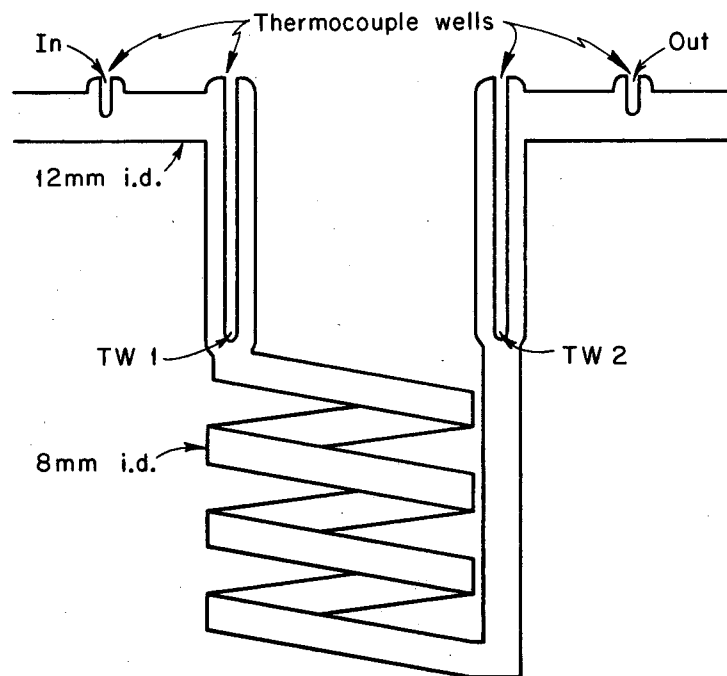
Fig. 9. Pyrolysis reactor (actual size).

connected to the apparatus by a tapered ground-glass joint. The remainder of the liquid products was collected in a trap immersed in a dry-ice-acetone bath in a Dewar flask. The remaining gases were exhausted to the hood. The amount of product collected by the first condenser varied from 50 to 75% of the total product depending upon flow rates used.

The temperatures of the reactant stream in the preheat section and reactor were measured by nine chromel-alumel thermocouples and were recorded on both a 12 point Brown Electronik milivolt recorder and a single channel Sargent, model SR, recorder.

The product was analysed using a Wilkens, model A-90P-2, Gas Chromatograph with a Brown recorder which was equipped with a Disc Integrator. The column used was a 5 ft. by 1/4-in. stainless steel tube packed with 0.25% M-phenyl ether-5 ring on 170/230 glass beads. The temperature of the column was maintained at 95° C and helium carrier gas at a flow rate of 16 ml/min was used. A sample chromatogram is shown in Fig. 10. The qualitative product gas analyses were carried out by injecting a 2 cc reactant effluent gas sample into the chromatograph via the gas sampling valve. A 5 ft. by 1/4 in. silica gel packed stainless steel column maintained at 40° C with a nitrogen carrier gas was used.
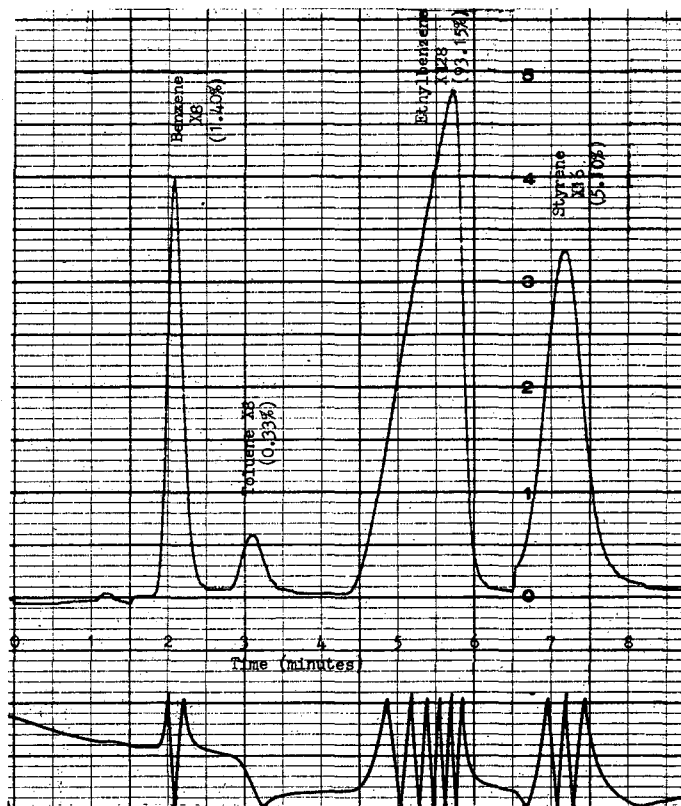
MU-35240

Fig. 10. Typical Chromatogram, run No. 72.

B. Reactants

The oil-pumped nitrogen used in attaining steady state operating conditions was purchased from the Liquid Carbonic division of General Dynamics. The prepurified nitrogen, with a minimum purity of 99.996% and a typical oxygen content of 9 ppm, was obtained from the Matheson Company. The oxygen, with a minimum purity of 99.6%, was also purchased from Matheson.

The ethylbenzene, which was purchased from both Eastman Organic Chemicals and Matheson, Coleman, and Bell, upon analysis by gas chromatography was found to contain small quantities of benzene and toluene. These impurities were removed by fractional distillation performed under a nitrogen atmosphere to avoid dissolution of oxygen in the ethylbenzene.

Table C.1. Data, pyrolysis runs without oxygen.

Run no.	Temperatures (°C)					EB Flow at 25° gm/sec	Rate at T_{iso} cc/sec	Product analysis				N_2 Flow at 25° cc/min	Rate at T_{iso} cc/sec	Total Flow cc/sec	EB Conc. gm/cc × 10⁴	Res. time sec.
	In	TW1	TW2	Out	T_{iso}			Styrene pph	Styrene %	Toluene pph	Benzene pph					
62	440	562	623	438	599	.0243	16.4	1.47	1.44	.04	.53	10,000	584	600	.405	.0833
63	419	555	621	417	596	.0294	19.8	1.06	1.05	.04	.21	10,000	582	602	.488	.0830
64	440	588	673	462	645	.0251	17.8	6.6	6.1	.22	1.70	10,000	615	633	.397	.0789
65	438	583	664	478	636	.0365	25.7	5.5	5.15	.22	1.35	10,000	608	634	.576	.0789
66	431	569	659	482	630	.0556	38.9	3.28	3.14	.11	.83	10,000	605	644	.833	.0776
67	438	562	654	490	625	.0880	61.2	1.80	1.76	.08	.50	10,000	602	663	1.327	.0754
68	424	574	671	473	642	.0515	36.5	7.65	6.95	.30	1.53	7,000	408	445	1.157	.1123
69	417	546	654	492	623	.0850	58.8	1.38	1.26	.06	.33	12,000	756	815	1.043	.0613
70	---	582	680	496	650	.0648	46.3	8.30	7.49	.35	2.15	10,000	626	672	.964	.0744
71	---	583	678	504	649	.0765	54.6	6.75	6.21	.35	1.64	10,000	626	681	1.123	.0734
72	---	575	678	504	647	.0905	64.5	5.47	5.10	.33	1.41	10,000	624	689	1.313	.0726
73	426	550	625	431	598	.0570	38.4	.56	.56	T	.21	10,000	592	630	.905	.0794
75	384	552	620	438	590	.0304	20.3	1.12	1.10	T	.30	6,400	348	368	.826	.1359
76	376	520	624	443	592	.0340	22.7	1.05	1.04	T	.28	6,400	348	370	.919	.1351
78	417	536	642	475	610	.0575	39.3	.50	.50	T	.17	13,000	820	885	.663	.0565
79	443	563	644	475	629	.0702	49.1	1.93	1.88	.12	.53	8,050	473	522	1.345	.0958
80	431	539	633	485	604	.0963	64.7	.32	.32	T	.21	13,000	820	885	1.088	.0565
92	398	561	659	431	630	.0144	10.1	14.4	12.3	.50	2.14	5,100	280	290	.497	.1724
98	369	522	625	428	593	.0255	17.1	2.36	2.29	.10	.60	5,350	284	301	.844	.1661
104	405	534	625	440	596	.0490	33.0	.85	.84	T	.27	7,000	392	425	1.153	.1176
109	419	541	635	447	606	.0547	37.2	1.42	1.39	.07	.37	7,000	395	432	1.266	.1157

T = trace, not determinable quantitatively.
pph = parts per 100 part ethylbenzene, liquid volume.
All values at pressure of one atmosphere
Temperatures In, TW1, TW2, Out identified in Fig. 9.

Table C.2. Data, pyrolysis runs containing oxygen.

Run No.	Temperatures (°C)					EB Flow at 25° gm/sec	Rate at T_{iso} cc/sec	Product analysis				N_2 Flow at 25° gm/min	Rate at T_{iso} cc/sec	O_2 Flow at 25° cc/min	Rate at T_{iso} cc/sec	O_2/EB ×100 cc/cc	Total Flow cc/sec	EB Conc. gm/cc ×10⁴	O_2 Conc. cc/cc ×10³	Res. time sec.
	In	TW1	TW2	Out	T_{iso}			Styrene pph	Styrene %	Toluene pph	Benzene pph									
81	417	534	628	462	599	.0618	41.6	.60	.60	T	.21	10,000	573	2.5	0.12	.293	615	1.005	0.20	.0813
82	417	525	600	433	574	.0642	42.1	.24	.24	T	T	10,000	557	50	2.36	5.62	601	1.068	3.926	.0832
83	417	527	597	433	571	.0628	41.0	.08	.08	T	T	10,000	555	25.	1.18	2.81	597	1.052	1.976	.0838
84	424	550	656	478	624	.0618	42.8	4.42	4.19	.11	.93	10,000	589	50.	2.48	5.84	634	0.975	3.911	.0789
85	428	555	654	480	624	.0612	42.4	3.30	3.17	.10	.85	10,000	589	25.	1.24	2.94	632	0.968	1.962	.0791
86	414	541	633	464	604	.0617	42.0	1.10	1.08	T	.28	10,000	576	25.	1.21	2.91	619	0.997	1.954	.0808
87	417	543	633	462	604	.0602	40.9	1.52	1.49	T	.33	10,000	576	50.	2.43	5.98	619	0.973	3.925	.0808
88	417	538	628	452	599	.0433	29.2	1.14	1.12	T	.26	10,000	572	20.	.97	3.33	602	0.719	1.611	.0831
89	419	539	630	452	600	.0432	29.2	1.50	1.47	T	.29	10,000	573	40.	1.98	6.69	604	0.715	3.273	.0828
90	419	541	625	443	597	.0453	30.5	.87	.86	T	.25	10,000	571	2.5	.12	.40	601	0.754	.200	.0832
91	426	539	625	450	597	.0458	30.9	.98	.97	T	.27	10,000	571	10.	.49	1.60	602	0.761	.814	.0831
93	398	560	659	426	630	.0162	11.3	16.3	13.6	.51	2.72	5,100	280	17.	.85	7.57	292	0.555	2.911	.1712
94	395	560	659	431	630	.0158	11.0	15.0	12.7	.45	2.62	5,100	280	8.	.41	3.70	291	0.543	1.409	.1718
95	395	559	659	431	629	.0162	11.3	13.2	11.4	.45	2.52	5,100	280	2.2	.12	.99	291	0.557	.412	.1718
96	410	539	642	454	607	.0441	30.1	1.80	1.76	T	.43	10,000	572	11.	.54	1.79	603	0.731	.896	.0829
97	412	539	642	452	607	.0436	29.8	1.61	1.58	T	.42	10,000	580	5.	.25	.82	610	0.715	.410	.0820
99	376	522	625	428	593	.0265	17.7	3.10	2.98	.09	.68	5,350	284	8.5	.413	2.44	302	0.877	1.368	.1657
100	374	522	625	428	593	.0267	17.9	2.67	2.58	.08	.60	5,350	284	3.2	.155	.87	302	0.884	.513	.1656
101	454	572	668	487	638	.0798	56.3	4.56	4.32	.19	.90	10,000	602	31.	1.58	2.81	660	1.209	2.393	.0758
102	454	572	668	487	635	.0808	56.7	3.54	3.39	.15	.78	10,000	600	18.	.91	1.60	658	1.228	1.383	.0760
103	447	572	661	487	633	.0815	57.7	3.40	3.26	.12	.73	10,000	598	7.0	.35	.61	656	1.242	.534	.0762
105	405	534	625	440	596	.0486	32.7	1.94	1.90	T	.38	7,000	392	60.	2.92	9.07	427	1.138	6.838	.1276
106	414	534	625	440	596	.0490	33.0	1.73	1.69	T	.34	7,000	392	27.	1.31	4.06	426	1.150	3.075	.1174
107	410	534	625	440	596	.0480	32.3	1.52	1.49	T	.31	7,000	392	13.5	.63	1.91	425	1.129	1.482	.1176
108	412	534	625	440	596	.0579	32.2	1.07	1.06	T	.30	7,000	392	6.5	.32	.98	425	1.127	.752	.1176
110	419	541	635	447	606	.0529	36.0	3.08	2.97	.07	.54	7,000	395	70.0	3.44	9.56	434	1.219	7.93	.1152
111	414	541	635	447	606	.0536	36.5	2.44	2.37	.07	.46	7,000	395	30.0	1.48	4.06	433	1.238	3.42	.1155
112	412	539	635	447	605	.0540	36.7	1.88	1.84	.07	.41	7,000	395	14.5	.71	1.93	432	1.250	1.64	.1157
113	410	539	635	445	605	.0531	36.1	1.58	1.55	.07	.37	7,000	395	7.5	.37	1.02	431	1.232	.858	.1160

D. Isokinetic Temperature

Since the reaction occurred in a flow reactor with a temperature gradient between the inlet and outlet, it was necessary to calculate an "isokinetic temperature," or the temperature at which an equivalent amount of conversion would occur if the reactor were isothermal. This calculation was based on a modification of the method of Fabuss, et al.[32]

For the derivation of this procedure let the subscript o stand for initial (or TW1), f stand for final (TW2), and i represent the isokinetic values. If we divide the Arrhenium expressions for the actual and isokinetic temperatures, the following expression results,

$$k/k_i = \exp[-E/R(1/T - 1/T_i)] = \exp\left[\frac{E}{R} \frac{(T-T_i)}{TT_i}\right] \tag{39}$$

For small temperature variations over the length of the reactor Eq. (39) may be approximated by

$$k/k_i = \exp\left[\frac{E}{R} - \frac{(T-T_i)}{T_i^2}\right] \tag{40}$$

If we assume that T is linear in the age of fluid in the reactor and if the conversion level is low, we have by the definition of T_i and k_i,

$$\frac{1}{T_f - T_o} \int_{T_o}^{T_f} \frac{k}{k_i} \, dT = 1 \tag{41}$$

Substituting Eq. (40) into Eq. (41) results in

$$(T_f - T_o) \exp(E/RT_i) = \int_{T_o}^{T_f} \exp(ET/RT_i^2) \, dT \tag{42}$$

Integrating and rearranging Eq. (42) we have,

$$\frac{(T_f - T_o)}{T_i} = \frac{RT_i}{E} \left\{ \exp\left[\frac{E}{RT_i} \frac{(T_f - T_i)}{T_i}\right] - \exp\left[\frac{E}{RT_i} \frac{(T_o - T_i)}{T_i}\right] \right\} \tag{43}$$

Let us define new dimensionless variables,

$$a = (T_i - T_o)/(T_f - T_o) \tag{44}$$

$$b = RT_i/E \tag{45}$$

$$d = (T_f - T_o)/T_i \tag{46}$$

Substituting these variables into Eq. (43), then:

$$d = b\left[\exp\left(\frac{d(1-a)}{b}\right) - \exp(-ad/b)\right] \tag{47}$$

Rearranging the above expression results in,

$$\exp(-ad/b) = d/b\left[\exp(d/b) - 1\right]^{-1} \tag{48}$$

Let us define another dimensionless variable,

$$h = d/b = \frac{(T_f - T_o)\,E}{RT_i^2} \tag{49}$$

Then,

$$\exp(-ha) = h\left[\exp(h) - 1\right]^{-1} \tag{50}$$

Taking natural logarithms and rearranging, we arrive at our final expression for the calculation of the isokinetic temperature:

$$a = \frac{\ln[\exp(h) - 1] - \ln(h)}{h} \tag{51}$$

This expression necessitates a solution by the method of successive approximations, but is rapidly convergent.

As mentioned in the main body of this report, this method involves many assumptions and approximations which are not rigorously valid. We

believe that the isokinetic temperature calculated from the above expression is as accurate as any which might be calculated using the available data.

E. Sample Calculations

1) Isokinetic temperature, T_i. Data from run 62

$$a = \frac{\ln [\exp(h) - 1] - \ln(h)}{h} \tag{51}$$

where

$$h = \frac{(T_f - T_o) E}{RT_i^2} \tag{49}$$

and

$$a = (T_i - T_o)/(T_f - T_o) \tag{44}$$

$T_o = TW1 = 562^{\circ} C = 835^{\circ} K$

$T_f = TW2 = 623^{\circ} C = 896^{\circ} K$

$E = 70,000$ cal/gm-mole

$R = 1.987$ cal/gm-mole $^{\circ}K$

For an initial value for T_i, use $(T_f + T_o)/2 = 865^{\circ} K.$

$$h = \frac{(896 - 835) (70,000)}{(1.987)(865)} = 3.08$$

Substituting into Eq. (51) we have,

$$T_i = \frac{\ln \ \exp(3.08) - 1 \ - \ln (3.08)}{3.08} \ (T_f - T_o) + T_o$$

$$T_i = (0.62)(61) + 835 = 872^{\circ} K = 599^{\circ} C$$

If the above calculations are made using the above value for T_i it may be seen that 872° K is the solution of Eq. (51) for run No. 62.

2) Ethylbenzene flow rate through the reactor at T_i for run No. 62

  Measured EB flow rate = 0.0243 gm/sec
  EB flow rate at 872° K =

$$\frac{0.0243 \ (gm/sec) \ 22,400 \ (cc/mole \ at \ 273^O \ K) \ 872^O \ K}{106.17 \ (gm/mole) \qquad\qquad 273^O \ K} = 16.4 \ cc/sec$$

3) Rate of styrene formation, for run No. 62

  Rate = conversion to styrene ethylbenzene flow rate
  ÷ reactor volume
  Conversion = 0.0144 moles/mole
  Ethylbenzene flow rate = 0.0243 gm/sec
  Reactor volume = 50 cc

$$Rate = \frac{(0.0144)(0.0243)}{(50)} = 0.0000700 \ (gm/cc\text{-}sec)$$

F. Nomenclature

A   = Frequency factor

E   = Apparent activation energy

(EB) = Ethylbenzene concentration

(O_2) = Oxygen concentration

R   = Gas constant

T   = Temperature

a   = Dimensionless temperature defined by Eq. (44)

b   = Dimensionless variable defined by Eq. (45)

d   = Dimensionless temperature defined by Eq. (46)

h   = Dimensionless variable defined by Eq. (49)

m   = Reaction order with respect to oxygen

n   = Reaction order with respect to ethylbenzene

Subscripts

f   = final

i,iso = isokinetic

o   = initial

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