

Lawrence Berkeley National Laboratory

Recent Work

Title

THE PYROLYSIS OF ETHYLBENZENE WITH AND WITHOUT OXYGEN INITIATION

Permalink

<https://escholarship.org/uc/item/6902h1ns>

Authors

Hausmann, Edwin D.
King, C. Judson.

Publication Date

1965-07-01

University of California

Ernest O. Lawrence Radiation Laboratory

THE PYROLYSIS OF ETHYLBENZENE WITH AND WITHOUT
OXYGEN INITIATION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE PYROLYSIS OF ETHYLBENZENE WITH AND WITHOUT
OXYGEN INITIATION

Edwin D. Hausmann and C. Judson King

July 1965

THE PYROLYSIS OF ETHYLBENZENE WITH AND WITHOUT OXYGEN INITIATION

Edwin D. Hausmann and C. Judson King

Lawrence Radiation Laboratory and
Department of Chemical Engineering
University of California
Berkeley, California

BRIEF

The effect of small quantities of oxygen (0 to 10%) on the thermal decomposition of ethylbenzene in the temperature range of 570-650° C was investigated utilizing a flow reactor with residence times on the order of 0.1 second. The runs made with oxygen excluded fit a half order rate expression with an activation energy of 69 kcal./g.mole. Small quantities of oxygen increase the rate of thermal decomposition but this effect tapers off as the oxygen concentration is increased. With an oxygen concentration of around 3% the same level of conversion is achieved at a temperature 10° C lower than that required when oxygen is excluded. The styrene yield selectivity increases from 74 mole % without oxygen to 81 mole % with 10% oxygen. The presence of oxygen also lowers the apparent activation energy.

SHORT SUMMARY

Rates of thermal decomposition of ethylbenzene were measured in an 0.1 second flow reactor at 570-650° C and interpreted via a Rice-Herzfeld mechanism. The effect of small quantities of oxygen on rate and product selectivity was determined.

THE PYROLYSIS OF ETHYLBENZENE WITH AND WITHOUT OXYGEN INITIATION

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 altering the reaction yield pattern. Vapors such as azomethane, diacetyl, diethyl ether, chloroform, dichloromethane, bromine, mercury, ethylene oxide, dimethylmercury, and oxygen have been found to have a homogeneous acceleration effect (4, 8, 13, 17, 20, 23). Economically and theoretically oxygen is of greatest interest. Oxygen is readily available at low cost and a knowledge of the mode of attack of oxygen upon hydrocarbons is fundamental to the understanding of hydrocarbon oxidation.

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. Traces of oxygen from the atmosphere will be found in all substances in which thermal decomposition would be undesirable.

A review of investigations of oxygen-initiated pyrolysis prior to 1956 has been given by Letort, who states that one part of oxygen in 100,000 doubles the initial decomposition rate of acetaldehyde at 477° C (13). Niclaude, Combe and Letort have shown that the pyrolysis threshold of acetaldehyde is 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 that the decomposition of n-butane is sensitized by the addition of small amounts of oxygen (14). 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 (21) and Engel, et al (5) prefer to attribute the drop in chain length to inhibition by olefinic products.

A detailed study of the reaction of n-butane and oxygen at low oxygen concentrations was reported by Appleby, et al (1). With 0.5% oxygen the rate of decomposition for longer residence times increased by a factor of 100. Engel, Combe, Letort, and Niclaude confirmed that trace quantities of oxygen accelerate the initial rate and lower the threshold temperature of the pyrolysis of n-butane (5). 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. Most previous workers have concluded that oxygen is a homogeneous accelerator; however Poltorak and Voevodskii suggest that oxygen initiation occurs as a surface reaction (18). They use their results for oxygen sensitized decomposition of propane to extend a theory of heterogeneous initiation of thermal decomposition reactions. In the present study a quartz reactor and a high partial pressure (about 1 atm.) of nitrogen diluent were employed to minimize surface effects.

The hydrocarbon investigated in this work was ethylbenzene. The thermal decomposition rates of alkylated aromatics have not been extensively studied under controlled conditions, and the effect of small amounts of added oxygen has not been reported for such compounds. In the case of ethylbenzene 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.

Most previous studies of the thermal decomposition of ethylbenzene have given only qualitative rate data. The reaction was first investigated by Berthelot, who, in 1869, passed gaseous ethylbenzene through an empty porcelain tube at a moderate red heat (3). A few experiments on the decomposition of ethylbenzene were made by Jost and Muffing using a static system (11). Webb and Corson determined the conditions at which the maximum yield of styrene could be obtained by pyrolytic dehydrogenation (24). Szwarc (22) and Esteban, et al (6) report quantitative measurements of the rate of the initial decomposition step, with the reaction chain suppressed by a carrier of toluene or aniline. Szwarc also gives qualitative results for the pyrolysis of pure ethylbenzene (22). Recent investigations of the pyrolysis of ethylbenzene have been reported by Lee and Oliver (12) and by Badger and Spotswood (2). 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 (10). 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. This raises the possibility that at a much lower oxygen content the selectivity of styrene formation might remain high without the simultaneous appearance of oxygenated aromatics which present a separation problem. Appleby, et al., reported a marked increase in the yield of olefins with the same carbon number from the pyrolysis of n-butane when a small amount of oxygen was added (1). A similar result for ethylbenzene could be of value commercially as an alternative to catalytic dehydrogenation.

ACQUISITION OF DATA

Equipment

The thermal decomposition studies were made using the apparatus shown schematically in Fig. 1. The 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 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. The reactor tube volume was 50 cm³. 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 as shown in Figures 1 and 2. Further details of the apparatus and accessory equipment may be found elsewhere (9).

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. 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 reactants 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.

After the run was completed the liquid product collected was weighed and a sample injected into a gas chromatograph equipped with a M-phenylether column at 95° C. The percentages of benzene, toluene, ethylbenzene, and styrene in the product were calculated from the resulting chromatogram. Oxygen and ethylbenzene concentrations in the reacting gas stream 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 concentration calculated from vapor pressure data. This percentage varied between 60 and 75% with variation of the nitrogen flow rate through the sparger-bottles. 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 at reactor conditions 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 flow rate from 960 mm Hg at a flow rate of 800 cc/sec to 860 mm at a flow rate of 400 cc/sec. True residence times in the reaction zone varied from 0.06 to 0.17 seconds. The temperatures at TW1 and TW2 (Figure 2) differed by from 60 to 100° C.

An "isokinetic" temperature was computed for each run by a modification of the method of Fabuss, et al (7). This introduces some uncertainty into the value of the average absolute temperature, but should have much less effect upon considerations based on the difference in temperature between runs.

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.

Measurements were then made using small quantities of oxygen. 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.

RESULTS AND DISCUSSION

Pyrolysis in the Absence of Oxygen

The data for pyrolysis without oxygen cover a temperature range from 590° to 650° C, with a three-fold variation of ethylbenzene concentration, and residence times of between 0.06 and

0.17 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 secondary reactions. The minimum conversion was 0.50% because of the difficulties in accurate analysis of smaller concentrations. Data are tabulated elsewhere (9).

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

	<u>Selectivity</u>
Styrene	74 \pm 3 mole %
Benzene	23 \pm 3
Toluene	3 \pm 1

This yield pattern showed no apparent trend with respect to reaction temperature or ethylbenzene concentration. Szwarc found these products in the approximate proportions 100:30-40:10-5 when the reaction chain was not suppressed (22).

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, ethane and ethylene were also 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 large amount of nitrogen diluent. Webb and Corson found approximately equal yields of ethylene and paraffinic hydrocarbons; however they employed much higher conversion levels where secondary reactions would be more important (24).

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

$$\text{Rate of conversion to styrene} = A \exp(-E/RT)(EB)^n \quad (1)$$

with a multiple regression utilizing the IBM 7094 computer.

The values of the parameters thus obtained and their standard errors of estimate are,

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

The standard error of the resulting correlation is 23%.

Figure 3 is a typical Arrhenius plot of the $1/2$ order rate constant,

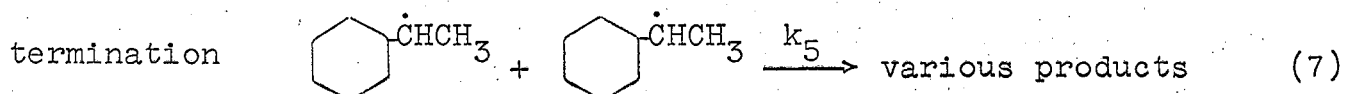
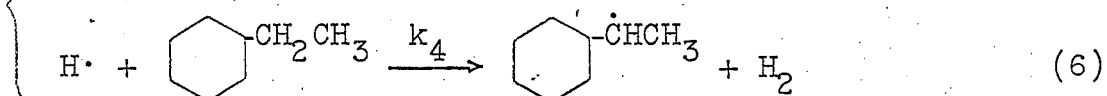
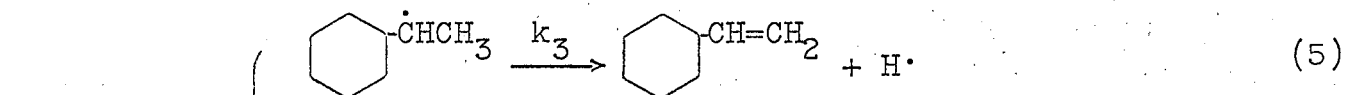
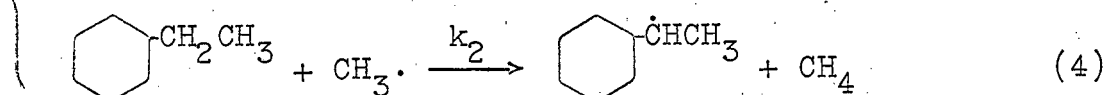
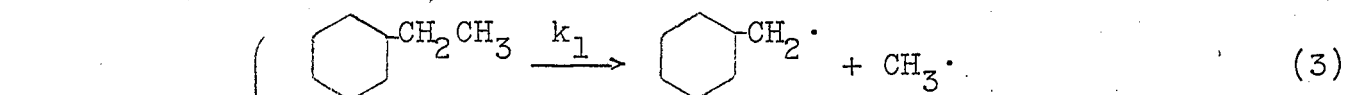
$$k_{1/2} = \text{rate to styrene}/(EB)^{1/2}, \quad (2)$$

plotted against the inverse of the absolute temperature. As can be seen the slope of this line is $35,000^\circ \text{ K}$, which corresponds to an apparent activation energy, E , of $70,000 \text{ cal/g-mole}$ and a frequency factor, A , of $3 \times 10^{13} \text{ (g-mole/cc)}^{1/2} \text{ (sec)}^{-1}$. The scatter of the data is due in part to the low conversion of the reactant at the lower temperatures which caused the product analysis to be less precise.

Figure 4 is a plot of the rate of styrene formation vs. the ethylbenzene concentration for nine selected runs. 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 uniform temperature of 600° C . As can be seen, Figure 4 substantiates the $1/2$ order with respect to ethylbenzene

as was determined with the use of the multiple regression analysis. Lee and Oliver (12) reported that the conversion of ethylbenzene to styrene appeared to be first order with respect to ethylbenzene at lower temperatures and appeared to approach zero order at higher temperatures. No trend of reaction order with respect to temperature was observed in the present work.

Rates of hydrocarbon pyrolysis have usually been interpreted through chain reaction mechanisms, following the original suggestion of Rice and Herzfeld (19). The following reaction mechanism is a logical possibility; 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/g-mole:



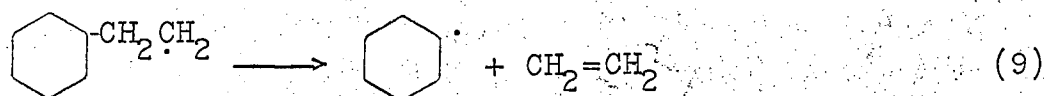
The benzyl radical is known to be unreactive (22); hence a benzyl radical initiation step similar to Reaction 4 has not been included.

If all the toluene produced is assumed to come from initiation by Reaction 3 the yield pattern analysis indicates chain lengths of 25 for the production of styrene. Even higher chain lengths result if toluene is also produced in a propagation reaction. Szwarc reported chain lengths of from 15-25 in the pyrolysis of ethylbenzene without chain suppression (22). With the long chain assumption, this mechanism results in the following expression for the rate of formation of styrene:

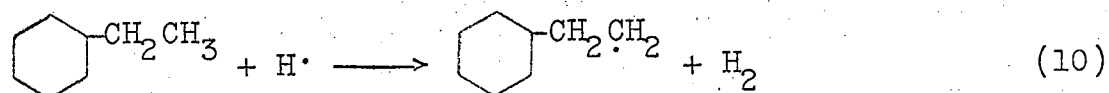
$$\text{rate to styrene} = \left[\frac{k_1 k_3^2}{2k_5} \right]^{1/2} (\text{EB})^{1/2} \quad (8)$$

The termination reaction chosen is logical since the extreme stability of the phenylethyl radicals provided by the several possible resonance forms afforded by the aromatic ring should allow these radicals to accumulate to a larger concentration than any of the other radicals which may be formed in the reaction. The termination represented by Reaction 7 imparts the reaction order of 1/2.

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

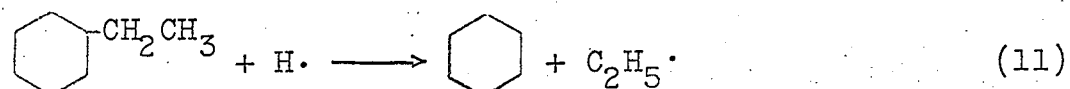


which would follow the abstraction of a primary hydrogen from ethylbenzene,



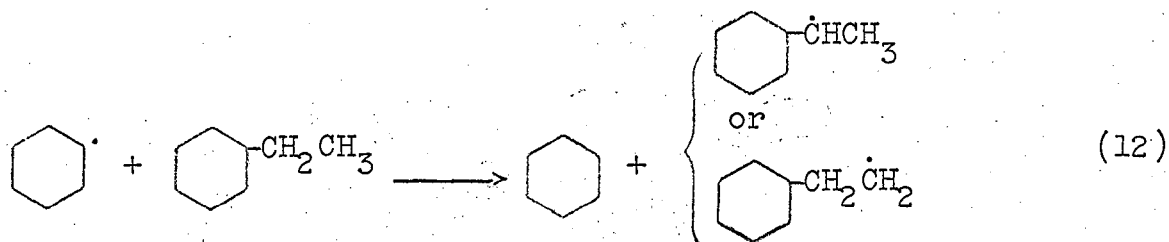
instead of the secondary abstraction shown in Reaction 6.

Benzene could also be formed by a variation of the second propagation step, such as that suggested by Szwarc (22):



A small amount of toluene may be formed by a modification of Reaction 11. A greater yield of ethylene than ethane was observed, but the ethyl radical from Reaction 11 could decompose to ethylene and a hydrogen atom instead of forming ethane through abstraction.

Benzene would be produced in Reaction 9 since β -scission occurs if this primary radical is formed and then decomposes. In Reaction 5 β -scission cannot occur since no β aliphatic C-C bond is available to break. If the benzene is formed largely by Reaction 9 the resulting phenyl radical will probably abstract hydrogen from ethylbenzene by a process similar to Reactions 4, 6 and 10:



Similarly Reaction 4 could lead to either of the two phenylethyl radicals. If Reactions 6 and 12 both produce the same ratio of the two phenylethyl radicals the rate expression for styrene formation, Eq. (8), will be unchanged. Similar reasoning

applies if benzene is produced by Reaction 11.

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 (21) may be taken for the individual steps in the mechanism. For k_1 , $E_1 = 63,000$ cal/g-mole and $A_1 = 10^{13}$ sec⁻¹ from Szwarc (22). For k_3 , $E_3 = 40,000$ cal/g-mole by analogy to similar reactions for other hydrocarbons (Ref. 21, p. 509); $A_3 = 10^{13}$ sec⁻¹, assuming a typical unimolecular type reaction. For k_5 , $E_5 = 0$ since it is a radical recombination reaction; $A_5 = 10^{14}$ cc/g-mole sec for a typical bimolecular reaction. Substitution of these quantities into the rate expression, Eq. (8), yields for an apparent activation energy, $E = 71,500$ cal/g-mole, and for the frequency factor, $A = 2 \times 10^{12}$ (cc/g-mole)^{1/2}(sec)⁻¹. This activation energy agrees well with the experimental value of 70,000 cal/g-mole. The frequency factor is a factor of 10 less than observed but the agreement is adequate if one considers that the values taken for A_3 and A_5 are only approximations.

Oxygen Initiated Pyrolysis

Figure 5 presents data obtained for pyrolysis of ethylbenzene with small amounts of added oxygen. This figure illustrates 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 were obtained by keeping all variables constant except for oxygen concentration, thereby minimizing possible errors. It may be

observed that the temperature for a given conversion level may be lowered about 10° C by adding about 0.03 moles of oxygen per mole of ethylbenzene. A detailed tabulation of runs made with added oxygen may be found elsewhere (9).

The results obtained in these studies correspond to the results obtained in the investigations of the oxygen initiated pyrolysis of n-butane, 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. The data in which a 100-fold increase in the rate of pyrolysis was observed were taken at a lower temperature (1).

No oxygenated hydrocarbons were detected in the analysis of the products from the runs with oxygen present, 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% (1). Not all of the oxygen which was added was consumed in the reaction; in fact very little of the oxygen which is added appears to have been consumed. For each mole of added oxygen between 0.06 and 0.35 moles of styrene were formed in addition to the conversion found in the absence of oxygen. A chain reaction based upon oxygen initiation suggests the formation of many molecules of styrene for every molecule of oxygen reacting.

The increase in reaction rate due to the introduction of oxygen was correlated to equation of the form of the law of mass action,

$$\text{rate}(\text{with } O_2) - \text{rate}(\text{without } O_2) = A \exp(-E/RT) (EB)^n (O_2)^m \quad (13)$$

by a multiple regression analysis where the rate due to straight pyrolysis was calculated from the previous correlation (Eq. 1).

The values of the parameters obtained are

$$A = 7.7 \times 10^9 \text{ (sec)}^{-1} (\text{moles/cc})^{0.28}$$

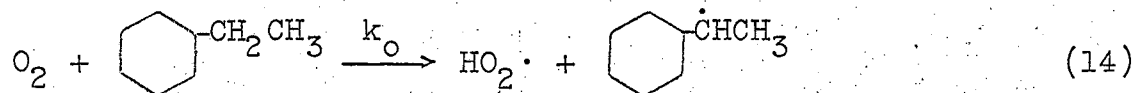
$$E = 48,500 \pm 1,600 \text{ cal/g-mole}$$

$$n = 0.02 \pm 0.59$$

$$m = 0.70 \pm 0.18$$

The activation energy of 48,500 cal/g-mole for the oxygen initiated portion of the pyrolysis is much lower than that for the pyrolysis without oxygen. Another interesting point is the near zero order with respect to ethylbenzene, although the probable error in this value is extremely large. The order of 0.7 with respect to oxygen compares with an order of 1/2 found by Appleby, et al. (1) 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 more likely, however, that the thermal pyrolysis and that due to oxygen share the same propagation chain. The chain initiating reactions would include both the thermal initiation given by Reactions 3 and 4 and an initiation step which includes oxygen, such as



If Reaction 14 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:

$$\text{rate to styrene} = \frac{k_3}{(2k_5)^{\frac{1}{2}}} (\text{EB})^{\frac{1}{2}} [k_o (\text{O}_2) + k_1]^{\frac{1}{2}} \quad (15)$$

Combining Eqs. (8) and (15) yields

$$\frac{\text{rate with oxygen}}{\text{rate without oxygen}} = [1 + \frac{k_o}{k_1} (\text{O}_2)]^{\frac{1}{2}} \quad (16)$$

Figure 7 presents a plot of the square of the ratio of the rate with oxygen to the rate without oxygen vs. the oxygen concentration. Following Eq. (16) 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.

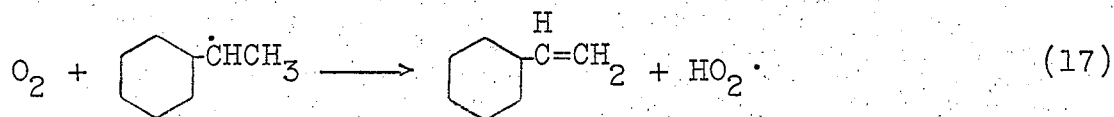
The form of plotting in Fig. 7 is highly sensitive to errors in the measured rates without oxygen. Figures 8a and 8b present a plot of the square of the rate vs. the oxygen concentration, as suggested by Eq. (15). In this case the relationship is less dependent on the rates in the absence of oxygen. Once again the data appear to fit straight lines at low oxygen levels, but taper 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 14 has a lower activation energy than Reaction 3. 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 leads to a difference of 13-21 kcal/g-mole between Reactions 3 and 14. If E for Reaction 3 is 63 kcal/g-mole as given by Szwarc (22), E for Reaction 14 is 42-50 kcal/g-mole. An activation energy of 40 kcal/g-mole for oxygen attack of this sort is indicated by Medley and Cooley (15). An activation energy of 45 kcal/g-mole for Reaction 14 yields a frequency factor for the same reaction of 3×10^{13} g-mole/cc sec, which is within the range normally encountered for bimolecular reactions.

A 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.

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



or



Hydroperoxy-radicals may be formed as intermediates in Reaction 17. Initially these reactions would have little effect, but as larger concentrations of oxygen are used these reactions could assume greater importance. Such inhibition reactions could cause the tapering off of the curves in Figs. 7 and 8. Because of the low conversion levels the present results indicate that the inhibition is due to oxygen itself rather than to the olefinic styrene product.

At 596° C the conversion of ethylbenzene is only 2% at the highest oxygen level. Product inhibition is not indicated at 2% conversion in the absence of oxygen.

As can be seen from Table I, the yield of styrene with respect to the total conversion increases with increasing oxygen concentrations 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 17, but it does appear that the styrene yield becomes elevated at oxygen contents below the points where curvature begins in Figs. 7 and 8. Alternative factors which could give an increased styrene yield include a higher selectivity for secondary hydrogen abstraction in Reaction 14 than in Reactions 4 and 6 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 (1) although the increase in selectivity is not as striking as found for n-butane.

If Reactions 14 and 17 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.

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 than 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 product inhibition. Oxygen increases the yield of styrene and decreases the yield of benzene but the increase is not great.

A $1/2$ order with respect to ethylbenzene is indicated for the pyrolysis of ethylbenzene in the absence of oxygen, with an activation energy of approximately 70,000 cal/g-mole.

In the evaluation of these results the warning of Steacie should be remembered (21): "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

This work was done at the Lawrence Radiation Laboratory under the auspices of the U. S. Atomic Energy Commission.

Nomenclature

- A = Frequency factor
E = Apparent activation energy
(EB) = Ethylbenzene concentration
(O₂) = Oxygen concentration
R = Gas constant
T = Temperature
m = Reaction order with respect to oxygen
n = Reaction order with respect to ethylbenzene

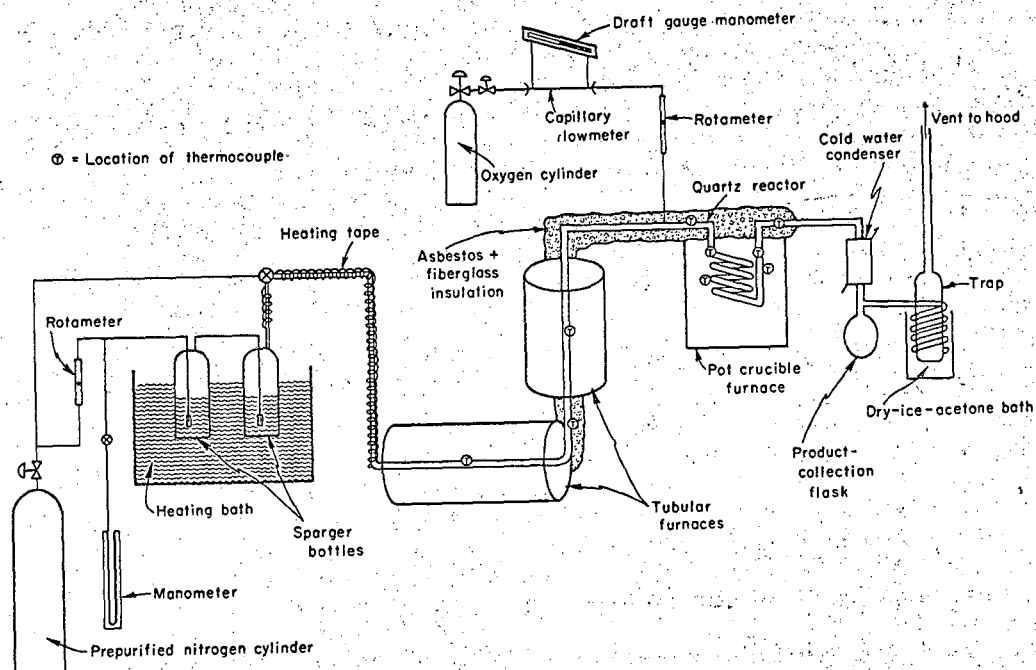
REFERENCES

1. Appleby, W. G., W. H. Avery, W. K. Meerbott and A. F. Sartor, J. Am. Chem. Soc. 75, 1809 (1953).
2. Badger, G. M. and T. M. Spotswood, J. Chem. Soc. (London) 1960, 4420.
3. Berthelot, M., Ann. Chim. Phys. (4) 16, 156 (1869).
4. Echols, L. S. and R. N. Pease, J. Am. Chem. Soc. 61, 208 (1939).
5. Engel, J., A. Combe, M. Letort and M. Niclaude, Rev. Inst. Franc. Petrole Ann. Combust. Liquides 12, 627 (1957).
6. Esteban, G. L., J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc. (London) 1963, 3873.
7. Fabuss, B. M., J. O. Smith and C. N. Satterfield, Chem. Eng. 70, No. 8, 153 (1963).
8. Frey, F. E., Ind. Eng. Chem. 26, 198 (1934).
9. Hausmann, E. D. and C. J. King, U.S.A.E.C. Report UCRL-16021, Lawrence Radiation Laboratory, Berkeley, California (1965).
10. Jones, J. H., M. R. Fenske, D. G. Hutton and H. D. Allendorf, "Vapor Phase Oxidation of Aromatic Hydrocarbons," (A.C.S. Div. of Petr. Chem. Preprints, Cleveland, Ohio, 1960) p. C-5.
11. Jost, W. and L. V. Muffling, Z. Electrochem. 47, 766 (1941).
12. Lee, E. H. and G. D. Oliver, Ind. Eng. Chem. 51, 1351 (1959).
13. Letort, M., Chim. Ind. 76, 430 (1956).
14. Maizus, Z. K., V. G. Markovich and M. B. Neiman, Dokl. Akad. Nauk, SSSR, 66, 1121 (1949).
15. Medley, H. D. and S. D. Cooley, "Hydrocarbon Oxidation," Vol. 3, Advances in Petroleum Chemistry and Refining, K. A. Kobe and J. J. McKetta, ed., (Interscience, New York, 1960) Chap. 7.

16. Niclause, M., A. Combe and M. Letort, J. Chem. Phys. 49, 605 (1952).
17. Norrish, R. G. W. and J. H. Purnell, Proc. Roy. Soc. (London) A243, 435 (1958).
18. Poltorak, V. A. and V. V. Voevodskii, Zh. Fiz. Khim. 35, 176, 284 (1961).
19. Rice, F. O. and K. F. Herzfeld, J. Am. Chem. Soc. 56, 2472 (1934).
20. Rice, F. O. and O. L. Polly, Trans. Faraday Soc. 35, 850 (1939).
21. Steacie, E. W. R., Atomic and Free Radical Reactions (Reinhold Publishing Corporation, New York, 1954) Chaps. I-IV, VI.
22. Szwarc, M., J. Chem. Phys. 17, 431 (1949).
23. Usov, Yu. N., E. V. Skvortsova, N. I. Kuvshinova and L. A. Elovatskaya, J. Appl. Chem. (USSR) 34, 943 (1961).
24. Webb, G. A. and B. B. Corson, Ind. Eng. Chem. 39, 1153 (1947).

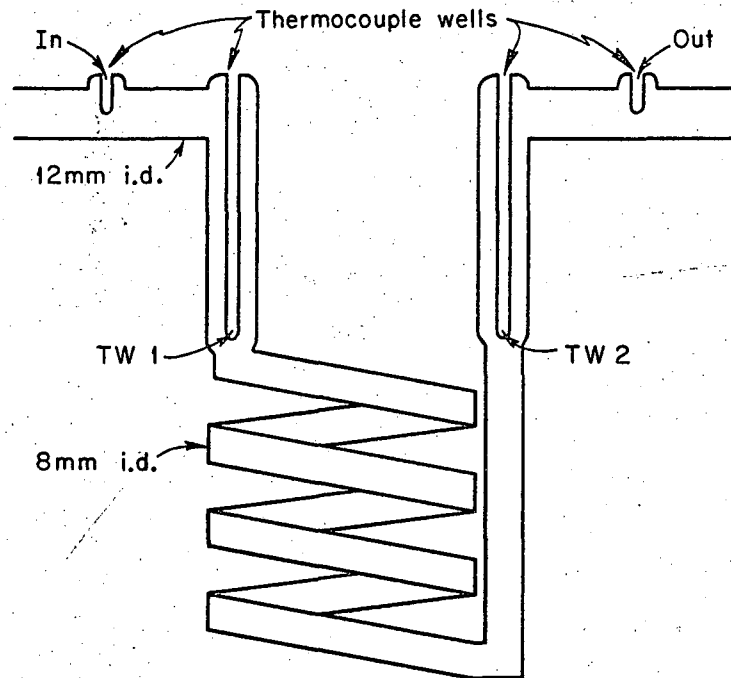
Table I. Effect of oxygen in the product yield pattern.

O_2/EB 100 (moles/mole)	T_{iso} (°C)	Product distribution (mole % of total conv.)		
		Styrene	Toluene	Benzene
0	593	73	3	24
0.9	593	76	2	22
2.4	593	76	2	22
0	596	72	Tr.	28
1.0	596	74	Tr.	26
1.9	596	80	Tr.	20
4.1	596	81	Tr.	19
9.1	596	81	Tr.	19
0.4	597	73	Tr.	27
1.6	597	74	Tr.	26
3.3	599	77	Tr.	23
6.7	600	80	Tr.	20
0	606	72	4	24
0.4	605	75	3	22
0.7	605	76	3	21
1.5	606	80	2	18
3.4	606	80	2	18
0	630	81	3	16
1.0	629	78	3	19
3.7	630	81	2	17
7.5	630	80	3	17



MU-33317

Fig. 1. Schematic diagram of pyrolysis apparatus.

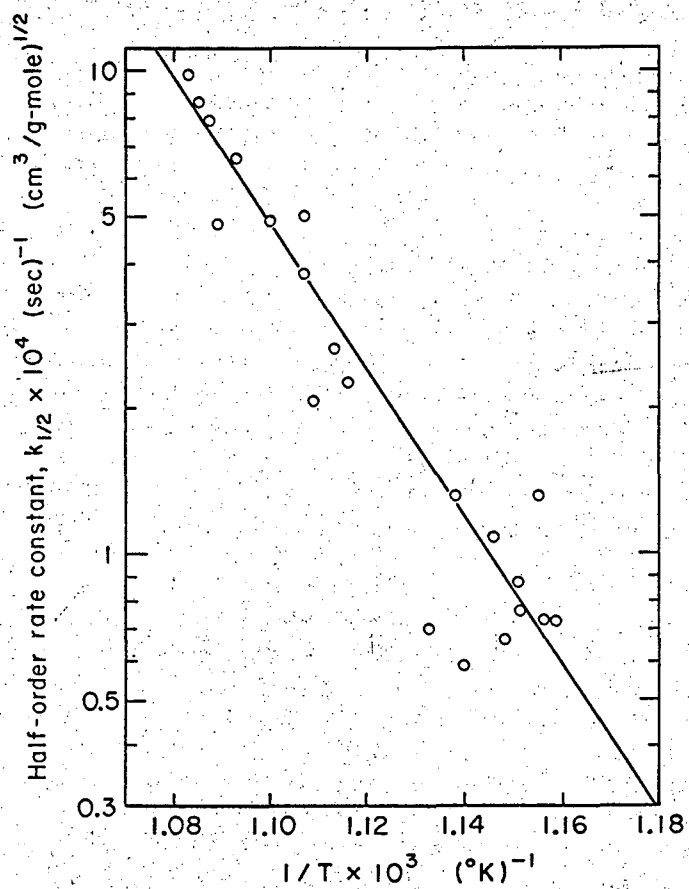


Overall length of tubing = 100 cm

Total internal volume of reactor = 50 cm³

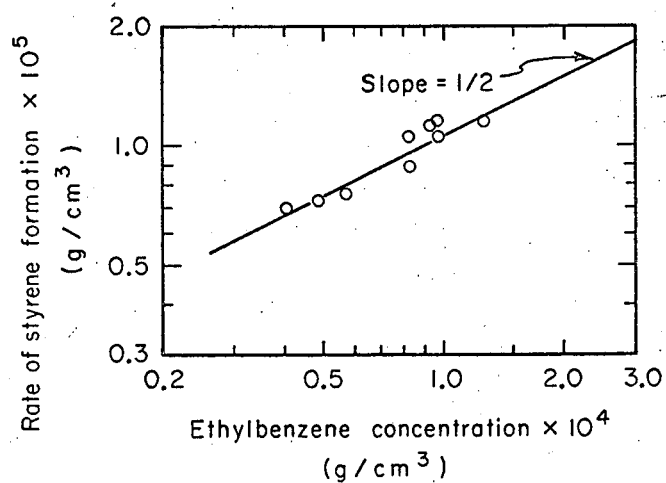
MU-35323

Fig. 2. Pyrolysis reactor



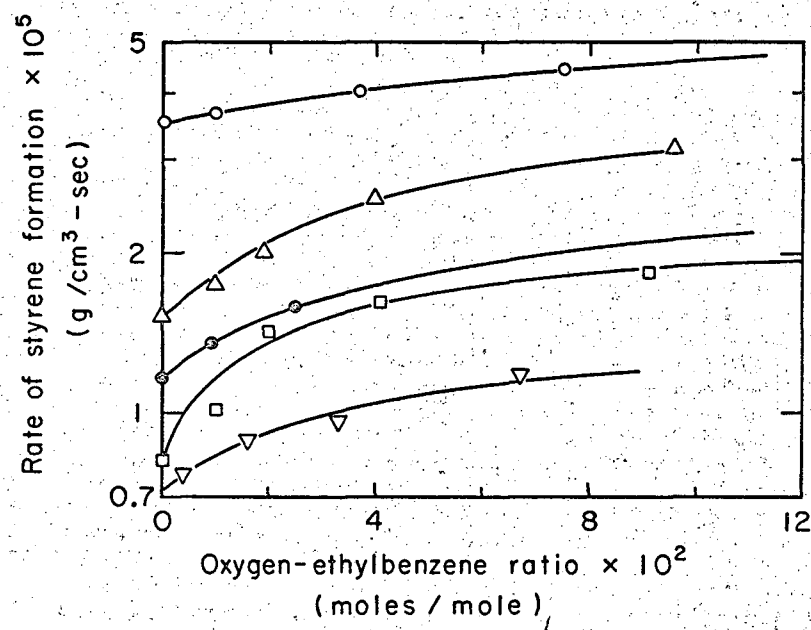
MU-35318

Fig. 3. Arrhenius plot for pyrolysis in the absence of oxygen.



MU-35319

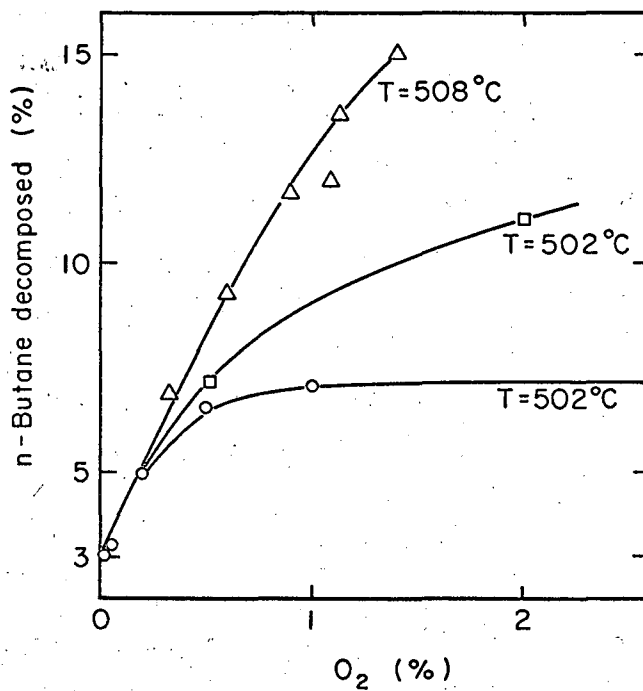
Fig. 4. Determination of order of reaction (the rate of styrene formation is corrected to 600° C).



MU-35320

Fig. 5. Effect of oxygen-ethylbenzene ratio on the rate of styrene formation.

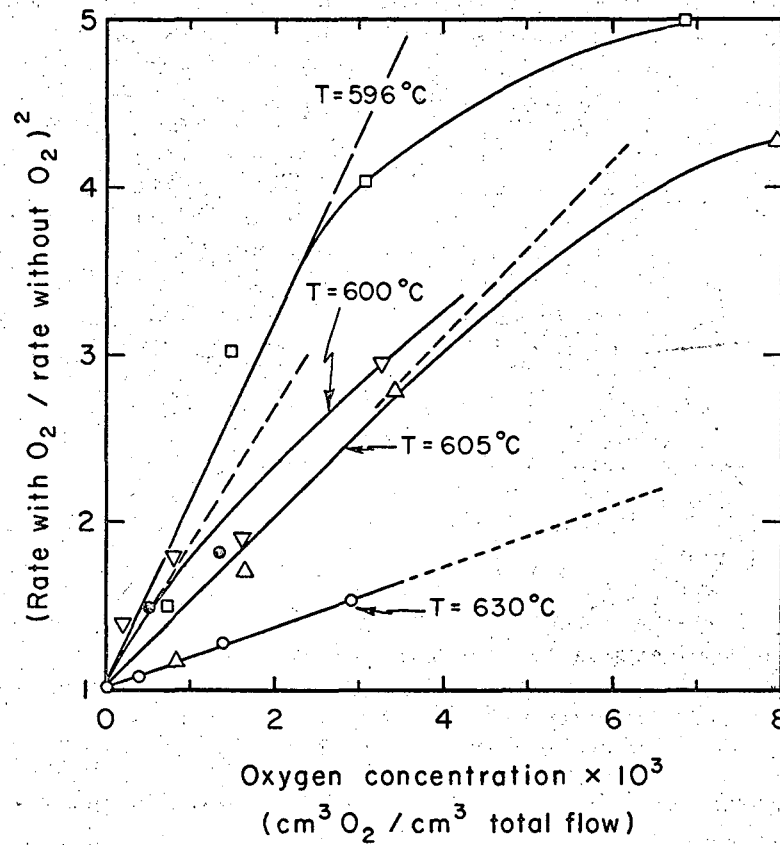
Temp.	Res. Time. (sec)	(EB) $\times 10^4$ (gm/cc)
▽ 600°C	0.08	0.7
□ 596°C	0.12	1.1
● 593°C	0.17	0.8
△ 605°C	0.12	1.3
○ 630°C	0.17	0.5



MU-35322

Fig. 6. Oxygen initiated pyrolysis of n-butane.

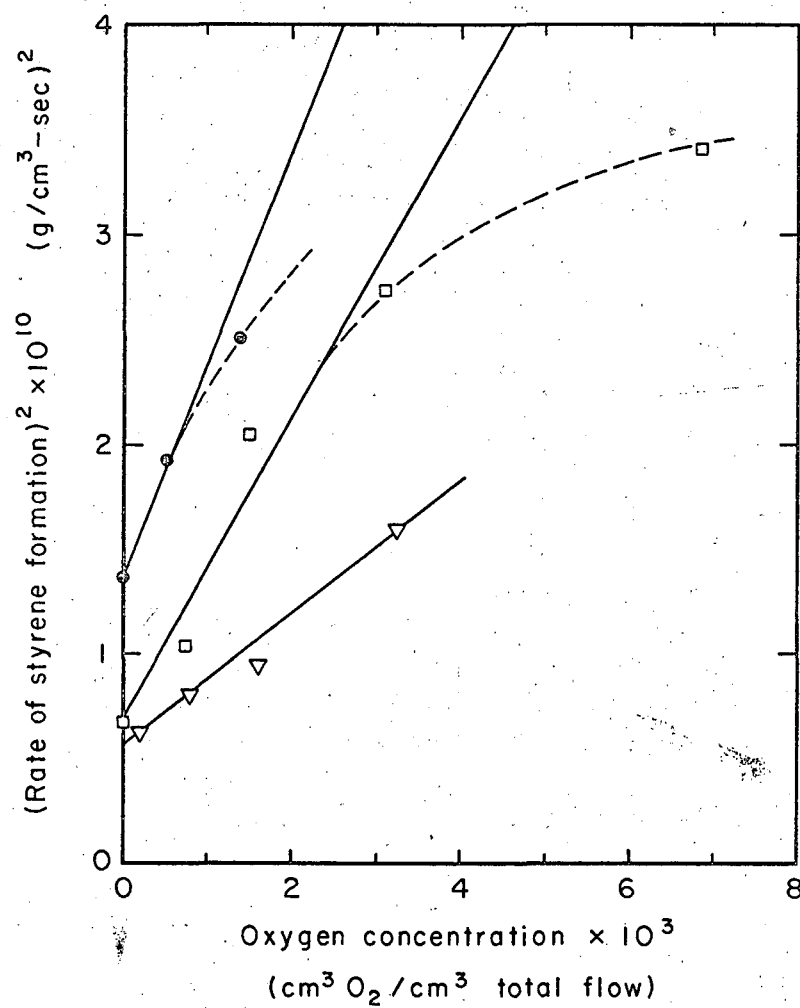
- Δ Rice and Polly $P_O = 298$ mm Hg. (20)
 ◻ Appleby, et al. $P_O = 380$ mm Hg. (1)
 ○ Maizus, et al. $P_O = 200$ mm Hg. (14)



MU-35352

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

Temp.	Res. Time (sec)	(EB) $\times 10^4$ (gm/cc)
∇ 600°C	0.08	0.7
\square 596°C	0.12	1.1
\odot 593°C	0.17	0.8
\triangle 605°C	0.12	1.3
\circ 630°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
\square 596°C	0.12	1.1
\odot 593°C	0.17	0.8

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

