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KINETICS OF THE THERMAL DECOMPOSITION  
OF BIPHENYL

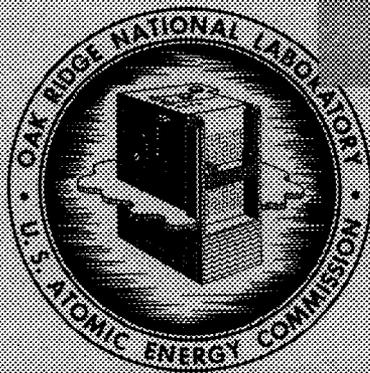
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### KINETICS OF THE THERMAL DECOMPOSITION OF BIPHENYL

*Note: These errata are printed on gummed paper so that they can be cut apart and glued directly into the report.*

Page 1. Cover the first two lines of the second paragraph with the lines below. (The rate expression is  $1.2 \times 10^{12}$  ... not  $10^{-12}$ .)

Page 9. Cover the first paragraph with the text below. (The descriptions of the two columns were interchanged.)

Page 26. Cover lines 6 and 7 of the second complete paragraph with the lines below. (Here again, the rate expression should be times  $10^{12}$ .)

ORNL-3602

Contract No. W-7405-eng-26

Reactor Chemistry Division

KINETICS OF THE THERMAL DECOMPOSITION OF BIPHENYL

L. B. Yeatts, Jr.

D. N. Hess

H. F. McDuffie

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MAY 1964

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## ABSTRACT

The initial rates of the thermal decomposition of pure biphenyl in the liquid phase were determined for the temperature range of 422 to 446°C. The products of pyrolysis were separated into three hydrocarbon fractions in a vacuum system and determined quantitatively by gas chromatographic procedures. The amount of biphenyl which had decomposed was found by difference.

If it is assumed that a first order rate law is valid, the rate at which biphenyl decomposes is given by the expression  $k = 1.2 \times 10^{12} \exp(-62,000/RT) \text{hr}^{-1}$ . The initial rates at which the four major products are formed, per mole of biphenyl, are: (1) hydrogen:  $0.58 \times 10^{-5}$  moles/hr at 422°C,  $1.9 \times 10^{-5}$  at 438°C, and  $2.7 \times 10^{-5}$  at 446°C; (2) benzene:  $1.1 \times 10^{-4}$  moles/hr at 422°C,  $3.1 \times 10^{-4}$  at 438°C, and  $4.8 \times 10^{-4}$  at 446°C; (3) terphenyls:  $0.71 \times 10^{-4}$  moles/hr at 422°C,  $2.0 \times 10^{-4}$  at 438°C and  $2.8 \times 10^{-4}$  at 446°C; and (4) quaterphenyls:  $0.25 \times 10^{-4}$  moles/hr at 422°C,  $0.77 \times 10^{-4}$  at 438°C, and  $1.3 \times 10^{-4}$  at 446°C.

The presence of water vapor in the biphenyl during pyrolysis had no noticeable effect upon the rates, whereas the presence of oxygen increased the rates by a factor of about two to four.

Results obtained by increasing the surface to volume ratio as much as a factor of 1000 for Pyrex and quartz surfaces indicated that the benzene yield reached a minimum value. Iron and stainless steel surfaces increased the rate of hydrogen formation tenfold.

A plausible mechanism is discussed for the uncatalyzed thermal decomposition, and suggestions are made for further work which would shed light on the detailed mechanism.

## 1. INTRODUCTION

Since the time of the Manhattan Project, reactor engineers have considered the possibilities of using organic hydrocarbons as a moderator, or a coolant, or a combination moderator-coolant in nuclear reactors. Interest along these lines increased in the early 1950's when enriched uranium became available. The probability of finding a compound with all the advantages of water, but having lower corrosion rate and vapor pressure, appeared good. This meant the reactor might be operated at a higher temperature, for the same pressure, with an accompanying increase in thermodynamic efficiency. Thus began an extensive research effort devoted to the selection of satisfactory organic compounds for practical reactor operation.

The prospective moderator-coolants were exposed to relatively high temperatures and radiation, simultaneously. Many classes of organic compounds, hydrocarbons and otherwise, were examined but only the aromatic hydrocarbons showed sufficient promise under these conditions to warrant further consideration for reactor development. Of this group, merely the polyphenyl compounds appear to be of potential value at this time.

Rather detailed data have been obtained by in-pile experiments on a mixture of terphenyl isomers and biphenyl (Santowax R)<sup>a</sup>, principally by workers at California Research Corporation<sup>(1)</sup>, Atomics International<sup>(2)</sup>, and AERE, Harwell, England<sup>(3)</sup>. The AI group has also conducted the Organic Moderated Reactor Experiment (OMRE) in Idaho. It is evident that both pyrolytic and radiolytic decomposition of the organic mixtures remain serious problems. Along with the destruction of the moderator-coolant at an

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<sup>a</sup>A product of Monsanto Chemical Company.

undesirable rate there is the accumulation of polymerized material which, through degradation, finally leads to fouling of the fuel elements.

If the chemical kinetics of the decomposition reactions were known, it is conceivable that methods might be found to retard or prevent the pyrolytic and radiolytic destruction of the organic moderator-coolant. Since those organic fluids of major interest at this time are all mixtures of compounds, interactions between the various intermediates and products present an extremely complex kinetic picture. Therefore, a simpler approach to the problem is to study the individual components of a prospective mixture.

De Halas<sup>(4)</sup> was one of the first investigators to undertake a study of this nature. He reported that several individual polyphenyl compounds, under the influence of heat or radiation, polymerize according to a first order rate law. The extent of reaction was determined from the amount of tar formation. Hall and Elder<sup>(5)</sup> presented G values and relative yields of products formed during the radiolysis of pure biphenyl at 74 to 82°C.

A paper by Gaumann and Rayroux<sup>(6)</sup> and a report by Kuper<sup>(7)</sup> present the results of recent studies of the pyrolytic chemistry of biphenyl and the terphenyl isomers. Kuper does not present data on the gaseous products since they generally represent less than 5% of the decomposition products. The temperature range studied was 400 to 440°C with the thermal decomposition ranging from about 0.2 to 20%. The work of Gaumann and Rayroux covers this same range of decomposition for biphenyl at 438, 458, and 472°C.

The studies at ORNL have been devoted to thermal degradation of biphenyl at 422, 438 and 446°C. The amount of biphenyl decomposed was held to less than 1.5% in order to simplify further the kinetics of decomposition and

to enable the identification of the principal initial products. The results reported are in better agreement with those of Gaumann and Rayroux than with those of Kuper. The effects of added surfaces, oxygen, and moisture upon the thermal decomposition are considered here also. These effects were not investigated in the previous work cited above.

## 2. EXPERIMENTAL PROCEDURE

### Sample Preparation

Chromatographically pure biphenyl was weighed into heavy-walled Pyrex glass ampoules which were closed at one end with a bubble breakseal. The ampoules were made from 5/8" O.D. (3/8" I.D.) tubing, were 7.5 cm long when sealed, and had a volume of 7 ml and a surface area of 25 cm<sup>2</sup>. The ampoules were treated overnight in a vacuum furnace at 500°C to remove adsorbed air and water vapor and cooled in a helium atmosphere before use. The ampoules were loaded with the desired quantity of biphenyl, attached to the vacuum line, and evacuated. The biphenyl was melted twice and evacuated each time to remove adsorbed air and moisture from it. After closing the stopcock to the vacuum line, a heat gun was used to melt the biphenyl which had collected on the cooled walls of the tube. Liquid nitrogen was employed to condense the biphenyl back into the ampoule. The ampoules were then sealed with the aid of a blowpipe.

### Pyrolysis

Thin-walled stainless steel bombs, containing the sealed ampoules of biphenyl, were preheated in a furnace for 1/2 hr at a controlled temperature, i.e., 400° for the 422°C experiments and 420° for the 438 and 446°C experiments. Under these conditions the decomposition of biphenyl during preheating was negligible.<sup>(7,8)</sup> The bombs were then transferred for

pyrolysis to a second furnace, regulated at a pre-set temperature. Use of the preheater made it possible to determine zero time more accurately, since the time lag in reaching the temperature of pyrolysis was reduced considerably. Aluminum blocks, drilled to fit the steel bombs closely, were used in both furnaces to increase the heat capacity of the furnaces and the rate of heat transfer, resulting in faster heating and more stable temperatures. The Chromel-Alumel thermocouple for furnace control was calibrated with a NBS calibrated thermocouple. A Speedomax H unit was used for temperature control ( $\pm 0.5^{\circ}\text{C}$ ) of the pyrolytic furnace. After the desired time interval, the bombs were removed from the furnace and quenched in air to halt the decomposition of the biphenyl. The time lag for quenching the reaction was nearly that found for heating the sample from the pre-heat temperature up to the temperature desired for pyrolysis.

#### Product Separation

In preparation for removal of the products, an extension tube with a side arm holding the nickel-breaker was sealed in place above the bubble break-seal. The assembly was connected to the vacuum system (Fig. 1), evacuated, and the breakseal broken. The ampoule, containing biphenyl and minute quantities of pyrolytic products, was heated with boiling water while the extension tube was cooled with ice water. The biphenyl and some of the polyphenyl products were vaporized from the ampoule and recondensed on the walls of the cooled extension tube. The benzene fraction was condensed upon passing those products more volatile than biphenyl through the U-tube traps immersed in liquid nitrogen. An automatic Toepler pump collected the gas fraction in a sample tube for analysis. When the gas collection was complete, the U-tube traps were closed off from the

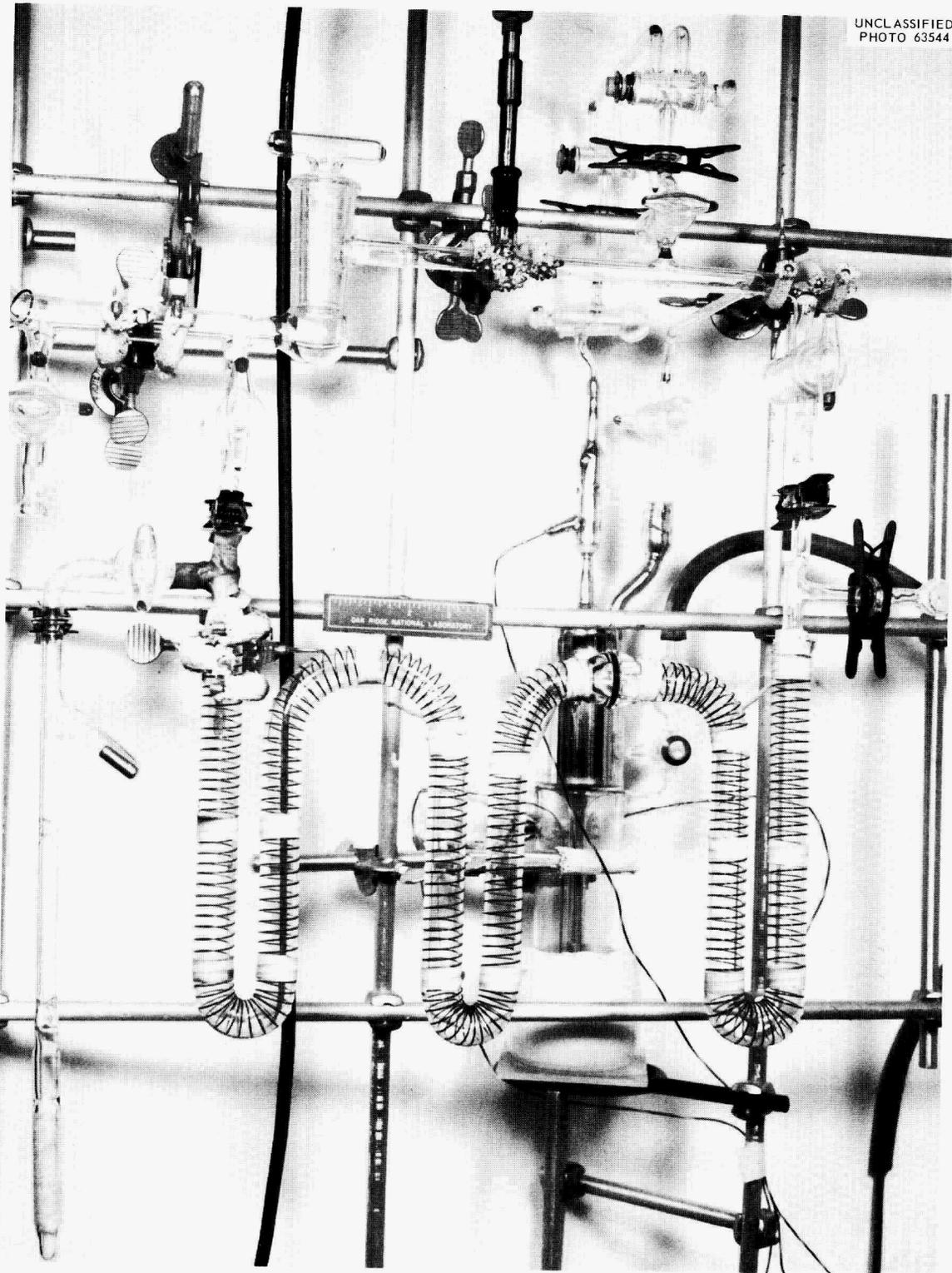


Fig. 1. Fractionation System for Products from Biphenyl Pyrolysis.

Toepler pump at one end and the ampoule at the other end, and the liquid nitrogen was removed from around these traps. The benzene fraction was vaporized and collected in a small tube, containing an appropriate volume of acetone, which was immersed in liquid nitrogen. The tightly stoppered glass tubes were stored in a refrigerator until the solution was analyzed. The biphenyl and polyphenyl products were recovered by removing the ampoule from the vacuum system and adding a known volume of benzene to serve as solvent. After the tube was stoppered, it was gently heated with heating tape so that most of the melted material ran into the benzene. The benzene solution was heated in a boiling water bath and gently shaken to dissolve the entire contents of the tube and ampoule. When the benzene solution cooled to room temperature, an aliquot was removed and stored for analysis in tightly stoppered glass tubes in a refrigerator.

#### Gas Analysis

The gas chromatograph used for the analysis of the gases was designed and assembled by the Instrument Department of the Instrumentation and Controls Division at Oak Ridge National Laboratory. A schematic diagram of the apparatus is shown in Fig. 2. Gow-Mac<sup>b</sup> constant current power supplies (Model 9999) were used with the thermal conductivity cells. The latter were detectors which employed matched thermistors with approximately 8000 ohms resistance. Detector No. 1 was operated with a bridge current of 4 ma; detector No. 2 at 6 ma. The bridge signal was received, attenuated, if necessary, and plotted by a 1 mv recorder with a 2-sec full-scale response. All of the electronic equipment was connected to a constant voltage transformer.

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<sup>b</sup>Gow-Mac Instrument Company, Madison, New Jersey.

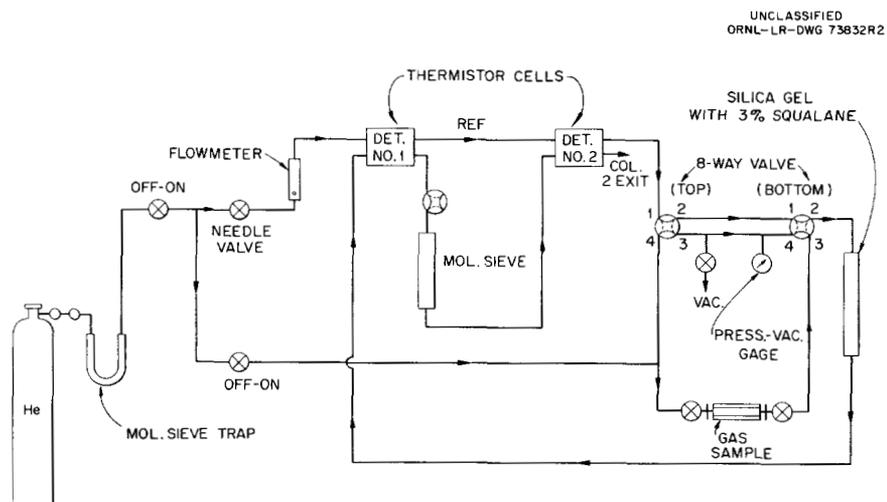


Fig. 2. Gas Chromatograph for Analysis of Gaseous Products from Pyrolysis of Biphenyl.

Copper tubing, 3/16 in. O.D. x 10 ft long, was used for columns after it had been cleaned with acetone and dried. Two columns in series were utilized: the first was filled with Burrell's<sup>c</sup> intermediate activity silica gel which had been heated overnight at about 250°C and treated with 3 wt % squalane. The second was packed lightly with 30-60 mesh molecular sieve (Linde 5A) and purged with dry helium at 300°C for at least four hours before it was put into service. The columns and detector blocks were completely immersed in a constant temperature bath regulated at  $21^{\circ}\text{C} \pm 0.02^{\circ}$ .

Tank helium was passed through a 1-in. x 12-in. stainless steel U-tube filled with molecular sieve (Linde 5A) for clean-up before entering the chromatograph. The carrier gas flowed through the reference side of the thermistor detector blocks in series before it reached the gas sampling section. This section was by-passed by means of an eight-way valve while attaching a gas sampling bulb. The eight-way and four-way valves used in the system were stainless steel precision valves with O-ring seals.<sup>d</sup> A soap-bubble flowmeter was attached when needed to the exit side of detector No. 2 in order to maintain the carrier gas flow rate at 40 ml/min with a helium back-pressure of 20 psi on the first column.

The permanent gases and methane passed through the first column unseparated and were resolved and determined by the molecular sieve column and detector No. 2. The low molecular weight hydrocarbons were resolved on the silica gel column and detected in detector No. 1. Since these latter gases passed into the molecular sieve column and were

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<sup>c</sup>Burrell Corporation, Pittsburgh, Pennsylvania.

<sup>d</sup>Circle Seal Precision Valves, Pasadena, California.

irreversibly adsorbed there, this column eventually became loaded and was replaced.

The retention times for the permanent gases and low molecular weight hydrocarbons resolved by this system are given in Table 1.

Table 1. Retention Times for the Permanent Gases and Low Molecular Weight Hydrocarbons

Gas	Silica Gel Retention Time (min)	Molecular Sieve Retention Time* (min)
H <sub>2</sub>		4.5
C <sub>2</sub> H <sub>6</sub>	5.1	
O <sub>2</sub>		6.1
N <sub>2</sub>		6.9
C <sub>2</sub> H <sub>4</sub>	7.8	
CO		9.7
CH <sub>4</sub>		11.2
C <sub>3</sub> H <sub>8</sub>	11.5	
C <sub>2</sub> H <sub>2</sub>	18.4	
C <sub>4</sub> H <sub>10</sub>	31.7	
C <sub>3</sub> H <sub>6</sub>	33.9	

\*Time from injection to detection.

Typical chromatograms produced by these gases are shown in Fig. 3.

The unresolved mixture of permanent gases and methane was eluted from the silica gel column first and appeared as a single large peak on the chromatogram. The presence of carbon dioxide in a sample was indicated by the shoulder on the propane peak. The unresolved mixture from this column was then separated on the molecular sieve column. The presence of

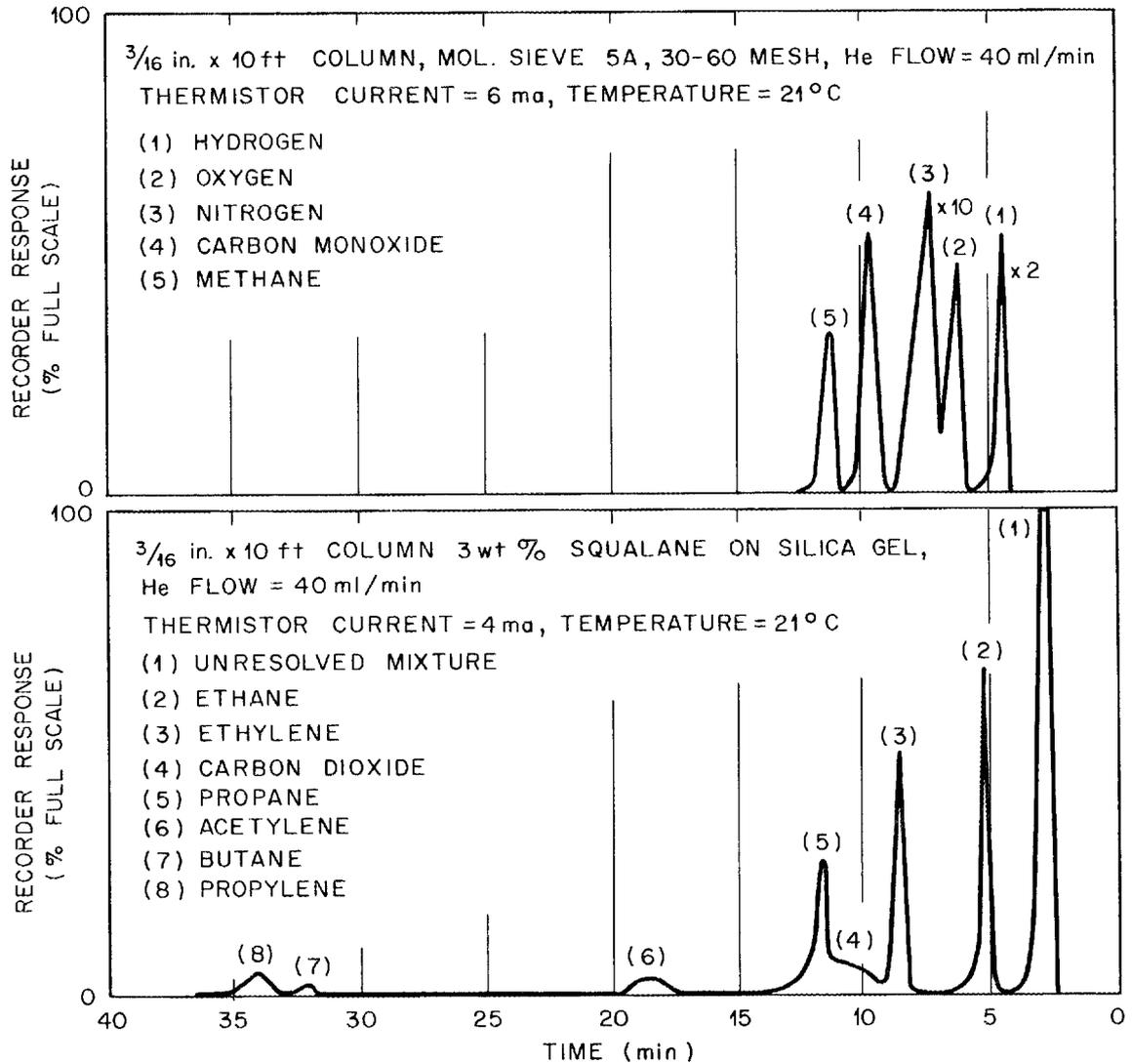
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Fig. 3. Chromatograms of Gaseous Products from Biphenyl Pyrolysis.

carbon monoxide and carbon dioxide implied the presence of some oxygen during the pyrolysis of biphenyl or diffusion of gases from the ampoule walls. Although the resolution of oxygen and nitrogen was incomplete, it was sufficient to indicate qualitatively the amount of leakage in the vacuum system during product fractionation. This leakage was decreased considerably as the research progressed.

The peak height measurements were used for the quantitative determination of the gaseous products since they proved to be more reproducible than peak area measurements. It was found that a straight line relationship existed between peak height and volume for each of these gases. The sensitivities, defined as the recorder response in scale divisions per unit volume of gas, are listed in Table 2. Analyses of the two gases of major interest in this work, hydrogen and methane, showed a precision of  $\pm 2\%$  and  $\pm 3\%$ , respectively, for a standard sample.

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Table 2. Sensitivities of the Low Molecular Weight Hydrocarbons, Hydrogen, and Carbon Monoxide

Gas	H <sub>2</sub>	CH <sub>4</sub>	CO	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>
Sensitivity (div/ $\mu$ l)	1.72	24.6	28.4	25.8	14.7	18.0	5.58

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#### Benzene Analysis

An F and M<sup>e</sup> Model gas chromatograph was employed in the analysis of benzene. The filament-type thermal conductivity cells were used with a

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<sup>e</sup>F and M Scientific Corporation, Avondale, Pennsylvania.

bridge current of 100 ma. The signal with proper attenuation was supplied to a 1 mv, 2 sec full-scale response recorder.

Cleaned copper tubing, 1/4 in. O.D. x 6 ft in length, was packed with 35-60 mesh Chromosorb P containing 30 wt % Apiezon L and 2 wt % Carbowax 20M as the stationary phases. The column packing was prepared by mixing the solid support with an ethanol solution of the Carbowax 20M, drying the mixture under a heat lamp, stirring it with a benzene solution of Apiezon L, and drying the product with the heat lamp. The tubing was tapped only lightly while it was being packed to eliminate the need for using a high back-pressure during column operation.

The flow rate of the helium carrier gas was 30 ml/min through the measuring side of the detector and approximately 15 ml/min through the reference side. The injection port and detector block temperatures were about 250°C while the column temperature was increased from 125 to 250°C at a rate of 11°C/min.

Standard solutions of benzene in acetone were used for calibration and were stored satisfactorily for weeks in a 25 ml graduate to which a Teflon bore stopcock was sealed. A silicone-rubber septum covered the short entry arm of the stopcock, which was opened only during sample removal. A detailed description of the storage vessel has been published<sup>(9)</sup>. Samples of the solutions were introduced into the chromatograph by syringe injection. The reproducibility of sample injection was

best when a gas syringe was used, and the volume of solution was measured with all of the liquid in the barrel. A pocket of air between the solution and the plunger permitted complete expulsion of the contents of the syringe into the injection port. If this was not done, solution remaining in the needle after injection was partially vaporized in the hot injection port; the fraction vaporized was variable and not measurable. As a result, precision would be poor.

Detailed procedures and data on analysis of benzene in mixtures with related compounds have been published<sup>(10, 11)</sup>. Benzene, with a retention time of 4.0 min, was the only compound detected in the fraction collected, as described earlier, in the liquid nitrogen traps. For the quantitative determinations, peak area measurements were found to be more accurate and precise than peak height measurements. A plot of benzene weight versus peak area produced a straight line from which the sensitivity was found to be 12.6 ( $\pm 2\%$ ) counts/ $\mu\text{g}$ . A Perkin-Elmer printing integrator Model 194 measured the peak areas of the components.

#### Polyphenyl Analysis

The F and M Model 500 gas chromatograph used for benzene analyses was used also for analysis of the polyphenyl fraction. Helium was used as the carrier gas at a flow rate of 100 ml/min through the measuring side of the detector block and approximately 15 ml/min through the reference

side. The injection port and detector block temperatures were about 350°C; the column temperature was increased from 150 to 375°C at a rate of 15°C/min. The bridge current was set at 100 ma.

The chromatographic column was a freshly cleaned 12-ft length of 1/4-in. O.D. stainless steel tubing, packed with 35-80 mesh Chromosorb P containing 20 wt % lithium chloride. The packing was prepared by dissolving the desired quantity of lithium chloride in water, intimately mixing the solution with the solid support, drying the mixture under a heat lamp, and finally heating it in a muffle furnace at 750°C for about one hour to fuse the salt onto the support<sup>(12)</sup>.

Standard solutions of the polyphenyl compounds in benzene were prepared and stored in the same type of container described in the previous section. Samples were injected into the chromatograph, also, as described earlier. Peak height measurements of these compounds were used for the quantitative determinations. The sensitivity was found to vary so widely during the course of a day that a standard sample was injected preceding and following the analysis of each unknown sample. The average sensitivity of these two analyses was used in the computations. The standard solution contained o-terphenyl, m-terphenyl, p-terphenyl, and 1,3,5-triphenylbenzene dissolved in benzene. Only one quaterphenyl was present in the standard solution because it was learned experimentally that there were only slight differences between the sensitivities of the quaterphenyl isomers. The retention times for the polyphenyl compounds available as standards are presented in Table 3.<sup>(13)</sup>

Table 3. Polyphenyl Retention Times on a LiCl Column

Compound	Formula	Retention Time (min)
Biphenyl	$C_6H_5-C_6H_5$	3.7
o-Terphenyl	$C_6H_5-C_6H_4-C_6H_5$	6.8
o-Quaterphenyl	$C_6H_5-(C_6H_4)_2-C_6H_5$	9.2
m-Terphenyl	$C_6H_5-C_6H_4-C_6H_5$	9.2
p-Terphenyl	$C_6H_5-C_6H_4-C_6H_5$	9.9
1,3,5-Triphenylbenzene	$(C_6H_5)_3-C_6H_3$	14.1
m-Quaterphenyl	$C_6H_5-(C_6H_4)_2-C_6H_5$	14.2
m,p-Quaterphenyl	$C_6H_5-(C_6H_4)_2-C_6H_5$	14.8
p-Quaterphenyl	$C_6H_5-(C_6H_4)_2-C_6H_5$	16.4

A chromatogram of the polyphenyl fraction of the pyrolytic products is shown in Fig. 4. Peak (4) was proven to be m-terphenyl rather than o-quaterphenyl by analysis of small samples at a low heating rate and a low flow rate. Although the difference between the retention times of m- and p-terphenyl was relatively small, there was sufficient time for complete resolution of these peaks under the operating conditions used. On the other hand, it was not possible to resolve m-quaterphenyl and 1,3,5-triphenylbenzene on this column. Hence, it cannot be stated unequivocally at this time that peak (8) was due to the presence of m-quaterphenyl. From relative retention time data<sup>(12)</sup>, peaks (6) and (7) are thought to be o,m-quaterphenyl and either o,p-quaterphenyl or 1,2,4-triphenylbenzene, but the lack of these compounds in pure form prevented positive identification.

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12-ft COLUMN, 20 wt% LiCl ON CHROMOSORB P; He FLOW = 100 ml/min  
BRIDGE CURRENT = 100 ma; TEMP PROGRAMMED AT 15 °C/min FROM 150-375 °C

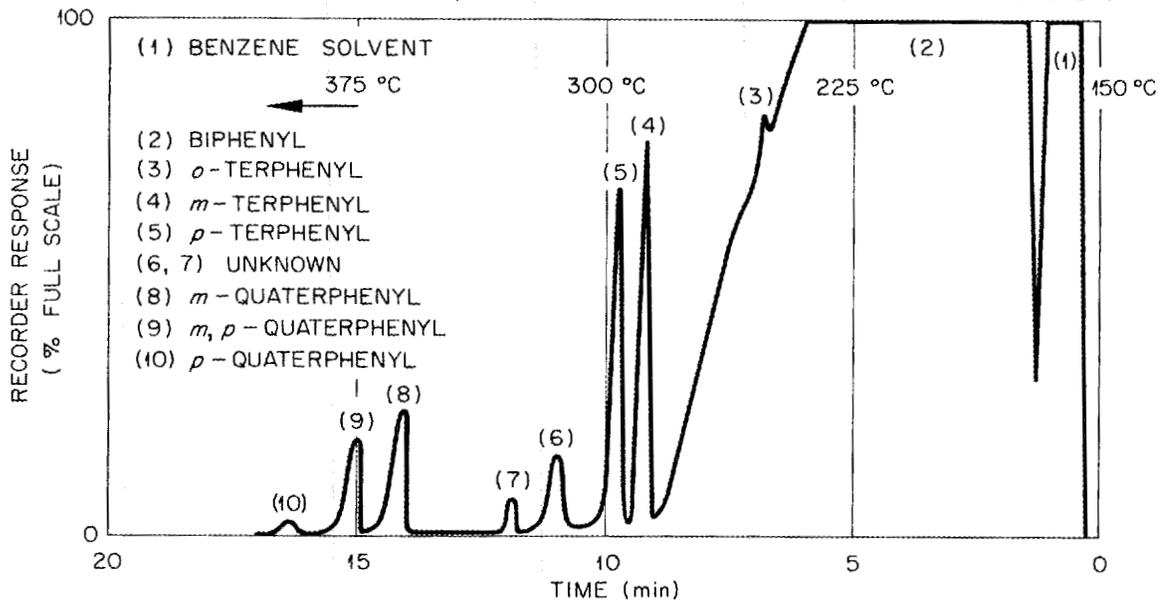


Fig. 4. Chromatogram of the Polyphenyl Products from Pyrolysis.

Chromatographically pure biphenyl was obtained from the California Research Corporation through the cooperation of R. O. Bolt. F. L. Howard, Pure Substances Section of the National Bureau of Standards, kindly supplied several polyphenyl compounds which were used as analytical standards.

A detailed review of the analytical procedures used in this project was published previously in a memorandum.<sup>(10)</sup>

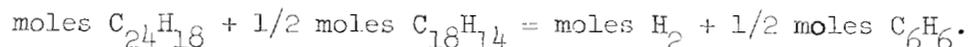
### III. RESULTS AND DISCUSSION

#### Net Reactions and Material Balance

On the basis of the analytical results, there are four major products formed, i.e. hydrogen gas, benzene, terphenyl isomers, and quaterphenyl isomers. The major net or overall reactions which were assumed to occur upon pyrolyzing biphenyl to produce these materials are:



These assumptions were tested by using reactions (1) and (2) to calculate the amount of hydrogen anticipated from the amounts of terphenyls and quaterphenyls produced. This value should equal the amount of the hydrogen gas determined plus one-half the amount found in the combined form as benzene. It follows from this that:



As seen in Table 4, good agreement was observed, indicating that the above equations were indeed the principal net reactions. The results which show a material imbalance will be discussed below.

Table 4

## Material Balance of Biphenyl Pyrolytic Products

(2.86 x 10<sup>-2</sup> moles Biphenyl)

Temp. (°C)	Time (hr)	Yield				Material Balance		Biphenyl Pyrolyzed (%)
		Hydrogen (moles)	Benzene (moles)	Terphenyls (moles)	Quaterphenyls (moles)	1/2 $\phi_3$ + $\phi_4$ (moles)	H <sub>2</sub> + 1/2 $\phi$ H (moles)	
		x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	
422	12	0.24	4.0	2.85	0.89	2.3	2.1	0.23
	24	0.38	7.2	4.99	1.25	3.8	4.0	0.48
	48	0.76	15.4	9.15	3.51	8.1	8.5	1.0
438	8	0.47	6.7	4.78	1.59	4.0	3.8	0.49
	12	0.70	11.0	7.09	2.96	6.5	6.2	0.77
	16	0.77	14.3	9.03	3.23	7.8	7.9	0.95
446	8	0.61	10.4	6.11	2.60	5.7	5.8	0.69
	12	0.95	16.8	9.73	4.72	9.6	9.4	1.1
5 x 10 <sup>-4</sup> moles H <sub>2</sub> O added								
422	12	0.21	3.1	3.12	0.71	2.2	1.8	0.27
2 x 10 <sup>-5</sup> moles O <sub>2</sub> added								
422	12	0.51	7.2	5.25	4.73	7.4	4.1	0.73

The percentage of biphenyl which was pyrolyzed can also be calculated for each experiment from the net reactions above. The degree of decomposition was limited to a low value in an effort to identify the initial products.

Variation of the Initial Rate of Reaction with  
Temperature

Liquid and vapor phase pyrolyses of equal amounts of biphenyl were performed under identical conditions of time (12 hr) and temperature (422°C) to ascertain the effect of physical state upon the rate of decomposition. The yield of benzene, the principal product, was twice as great for the vapor phase decomposition as for the liquid phase pyrolysis. That this was not a surface effect will be shown below. As a consequence of these results, the following liquid phase studies were made with a vapor space of less than 5% at the pyrolytic temperature.

The straight line relationship that exists between the average hydrogen yield and time at three different temperatures is shown in Fig. 5. Table 5 lists the initial rates of hydrogen formation.

Table 5. Initial Rates of Product Formation

(moles hr<sup>-1</sup> mole<sup>-1</sup> Biphenyl)

Product	Temperature			Relative Rates
	422°C	438°C	446°C	
Hydrogen (x 10 <sup>-5</sup> )	0.58	1.9	2.7	0.06
Benzene (x 10 <sup>-4</sup> )	1.1	3.1	4.8	1.0
Terphenyls (x 10 <sup>-4</sup> )	0.71	2.0	2.8	0.6
Quaterphenyls (x 10 <sup>-4</sup> )	0.25	0.77	1.3	0.25

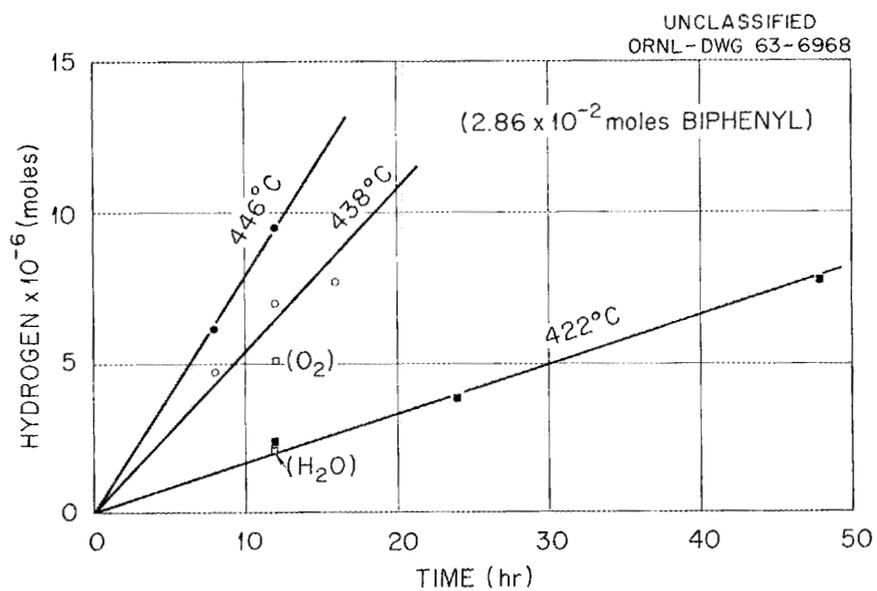


Fig. 5. Variation of Hydrogen Yield with Time.

The amount of methane formed during pyrolysis was roughly one-tenth the amount of hydrogen (see Appendix A). There appears to be no clear relationship between the methane produced and time. The other aliphatic hydrocarbons were present in amounts too small for precise quantitative determinations ( $1/10$  to  $1/100 \times \text{CH}_4$ ). Obviously, a benzene ring must be "cracked" and hydrogen in some form acquired to produce the low molecular weight hydrocarbons. Traces of oxygen might be expected to increase rupture of the ring structure. However, an experiment in which oxygen gas was present during pyrolysis showed little difference in the rate of methane production (see Appendix A). Possibly, the nature of the surface at the biphenyl-Pyrex glass interface accounts for this degradation path of lesser significance.

The variation of the average benzene yield with time at three different temperatures during the low percentage conversion of biphenyl is plotted in Fig. 6. Again, a straight line relationship exists. The initial rates of benzene formation are presented in Table 5. The value at  $438^\circ\text{C}$ ,  $3.1 \times 10^{-4}$  moles per hour per mole of biphenyl, is in fair agreement with a value of  $5.9 \times 10^{-4}$  moles per hour obtained by Gaumann and Rayroux.<sup>(6)</sup>

The variations of yields of terphenyls and quaterphenyls with time at three different temperatures are shown graphically in Figs. 7 and 8, and the resulting rates of formation are given in Table 5. The initial rate of terphenyl formation,  $2.0 \times 10^{-4}$  moles per mole of biphenyl per hour at  $438^\circ\text{C}$ , agrees fairly well with the Gaumann and Rayroux value of  $3.9 \times 10^{-4}$  for the same temperature. Their data yield a value of  $2.9 \times 10^{-4}$  moles of quaterphenyl per mole of biphenyl per hour at  $438^\circ\text{C}$

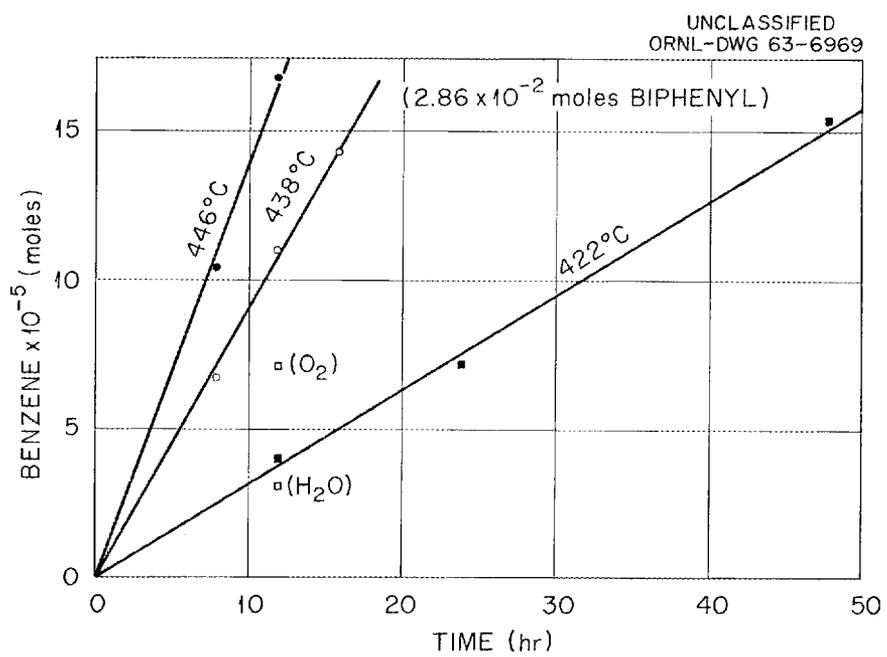


Fig. 6. Variation of Benzene Yield with Time.

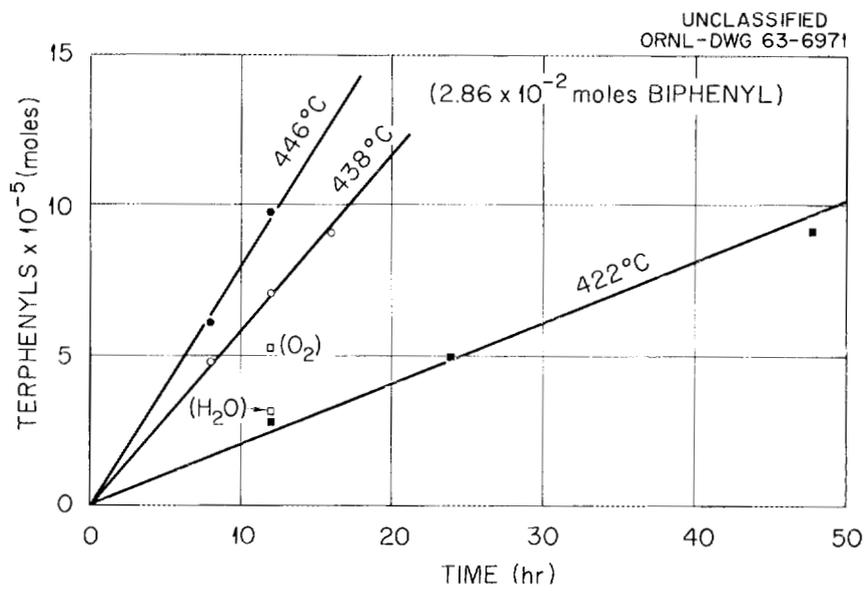


Fig. 7. Variation of Terphenyl Yield with Time.

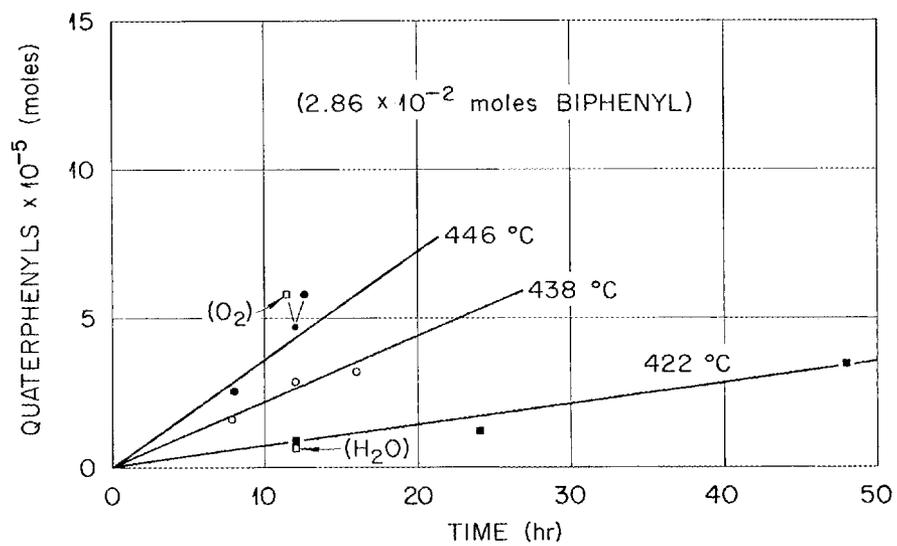
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Fig. 8. Variation of Quaterphenyl Yield with Time.

compared to  $7.7 \times 10^{-5}$  found in this research. The dependence of the average polyphenyl yields upon time is presented in Fig. 9. The polyphenyl yield is equal to the sum of the isomeric terphenyls and the isomeric quaterphenyls found as products (see Appendices). The initial rates at which the polyphenyls were formed (per mole of biphenyl) are  $9.3 \times 10^{-5}$  moles/hr at  $422^{\circ}\text{C}$ ,  $2.8 \times 10^{-4}$  moles/hr at  $438^{\circ}\text{C}$ , and  $4.0 \times 10^{-4}$  moles/hr at  $446^{\circ}\text{C}$ . Note that the initial rates at which benzene and polyphenyls are formed at these temperatures are nearly identical.

The graph in Fig. 10 shows that the rate at which biphenyl thermally decomposes is essentially first order at these temperatures for a low percentage decomposition. This agrees with the findings of others<sup>(6,7)</sup> who continued the decomposition to 20 mole percent.

Applying the Arrhenius equation to the data from the  $422$  and  $446^{\circ}\text{C}$  experiments, the value of the activation energy for hydrogen formation is about 65 kcal/mole; for benzene formation, about 61 kcal/mole; for terphenyl formation, about 56 kcal/mole; and for quaterphenyl formation, about 67 kcal/mole. The specific rate constant for the overall decomposition of biphenyl between  $422$  and  $446^{\circ}\text{C}$ , assuming a first order rate, is  $k = 1.2 \times 10^{12} \exp(-62,000/RT)\text{hr}^{-1}$ . Gaumann and Rayroux<sup>(6)</sup> report a value for the activation energy of approximately 66 kcal/mole for the thermal decomposition of biphenyl compared with values of 93 kcal/mole found by Kuper<sup>(7)</sup> and 74 kcal/mole by de Halas<sup>(4)</sup> for the same reaction.

#### Effect of Water and Oxygen Upon the Initial Rates

To investigate the possibility that the presence of traces of oxygen, in the form of water vapor or air, during pyrolysis might have a marked

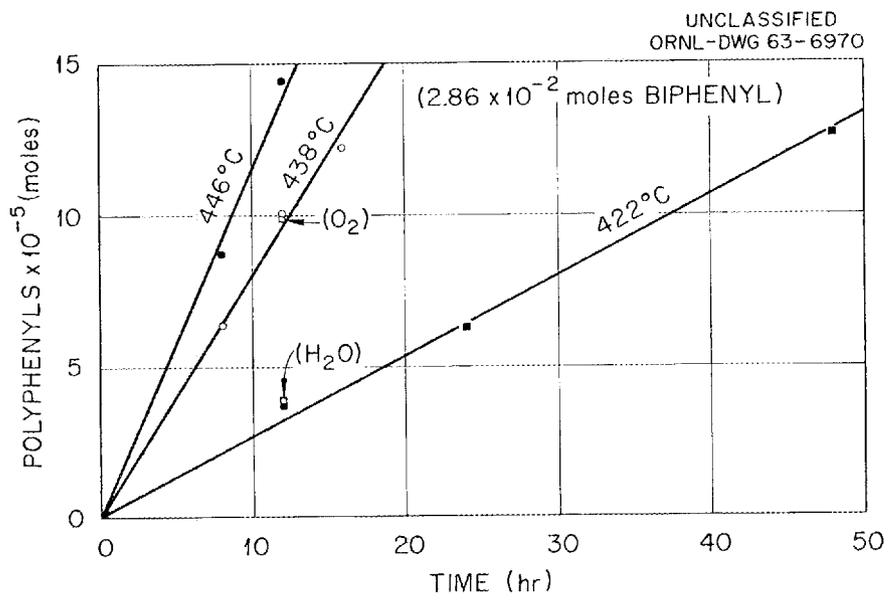


Fig. 9. Variation of Polyphenyl Yield with Time.

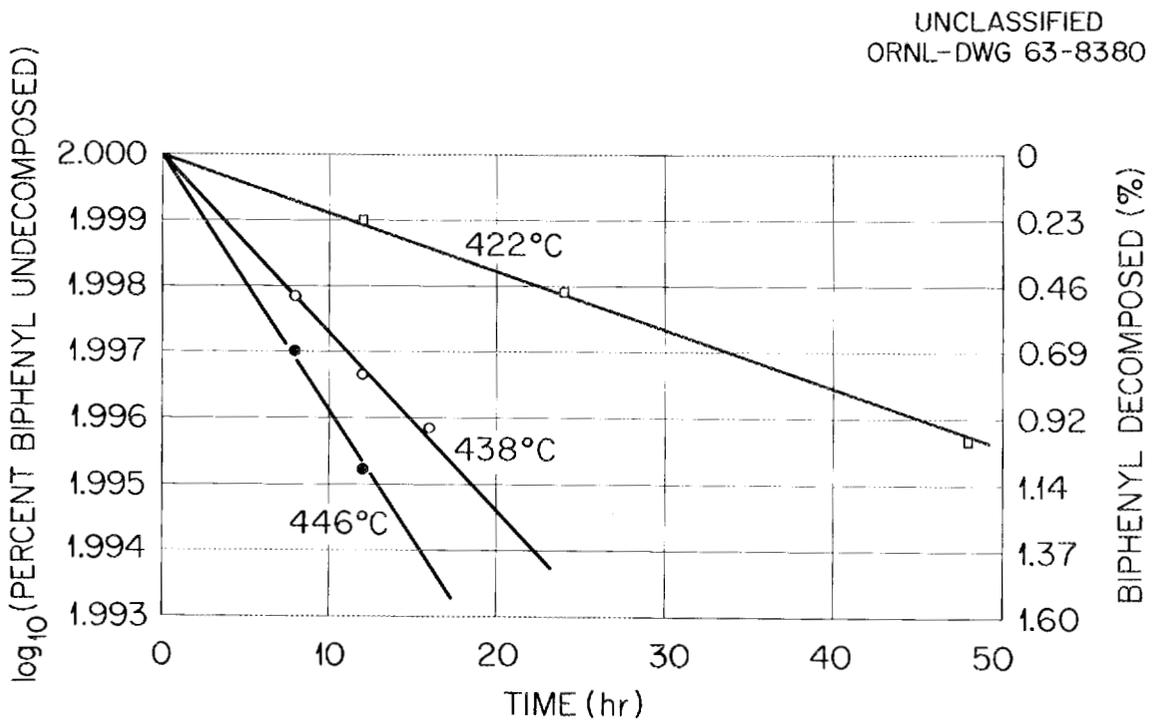


Fig. 10. Variation in Decomposition of Biphenyl with Time.

effect upon the initial rate of decomposition of biphenyl, the last two experiments presented in Table 4 were performed. It can be seen from these data and in Figs. 5 through 9 that the addition of  $5 \times 10^{-4}$  moles of water before pyrolysis had little or no effect upon the rate of formation of hydrogen, benzene, or polyphenyls during a 12 hr period at  $422^{\circ}\text{C}$ . The fact that a satisfactory material balance was obtained indicates little likelihood of the onset of any additional significant rate processes.

However, the addition of  $2 \times 10^{-5}$  moles of pure  $\text{O}_2$  before pyrolysis under the same conditions caused a marked increase in the rates of formation of all products. That this is particularly true in the case of the quaterphenyls can be seen in Figs. 5 through 9. As might be anticipated, the yield of carbon monoxide was great (see Appendix A). However, it was not high enough to account for all of the oxygen initially added. The lack of a material balance (Table 4) for this experiment can be attributed to the failure to determine experimentally all of the hydrogen produced in a combined form. It seems reasonable to believe that the oxygen and hydrogen which were not accounted for were in the form of water and organic oxygen compounds which would be undetected by our analytical procedures.

#### Effect of Added Surfaces Upon the Rate

To study the effect of high surface area and the type of surface upon the rate of product formation, the data shown in Table 6 were obtained. The initial rate studies were performed using Pyrex ampoules with a surface area of  $25 \text{ cm}^2$ . These results were used for the reference experiment and have been presented in Table 5. These values were corrected

Table 6

Material Balance for Biphenyl Pyrolysis in the Presence of Added Surfaces

(Conditions: 500 cm<sup>2</sup> Surface Area, 12 hr, 422°C, 1.95 x 10<sup>-2</sup> moles Biphenyl)

Surface	Yield				Material Balance		Biphenyl Pyrolyzed (%)
	Hydrogen (moles)	Benzene (moles)	Terphenyls (moles)	Quaterphenyls (moles)	1/2 O <sub>3</sub> + O <sub>4</sub> (moles)	H <sub>2</sub> + 1/2 O <sub>H</sub> (moles)	
	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	
Reference (25 cm <sup>2</sup> )	0.14	2.6	1.67	0.59	1.4	1.4	0.26
Pyrex	0.30	1.6	1.31	0.34	1.0	1.1	0.18
Quartz	0.14	2.0	1.31	0.34	1.0	1.1	0.19
Iron	1.2	2.3	2.06	0.52	1.6	2.4	0.28
Stainless steel	1.38	1.3	1.04	0.16	0.7	2.0	0.14
Quartz + SS (1:1)	1.60	1.8	1.35	0.39	1.0	2.5	0.20
Pyrex (2850 cm <sup>2</sup> )	0.22	0.72	-	-	-	-	-
Quartz (7000 cm <sup>2</sup> )	0.21	0.71	-	-	-	-	-

for the difference in the amount of biphenyl used, since the added materials occupied a part of the ampoule volume. The surface to volume ratio was varied from 3.6 in the first case to as high as 1000. This was done by adding the materials in the form of "wool" to the pyrolysis tubes, which were then baked out as described earlier. The presence of Pyrex and quartz surfaces had an appreciable effect only on the benzene yield.\* Further, it appears from the data in Table 6 that the yield of benzene reaches a minimum value as the surface area of Pyrex or quartz increases, but the value is independent of the nature of the surface. Although the data is not as conclusive for the yields of terphenyls and quaterphenyls, there seems to be a trend in the same direction for them also.

The yields of hydrogen and methane (see Appendix B) in the presence of iron surfaces were increased by factors of about 10 above the normal yield, whereas the amounts of benzene, terphenyls, and quaterphenyls remained unchanged. These particular results were obtained from the pyrolysis of a single sample in each instance. Therefore, differences less than an order of magnitude are probably best assigned to experimental error at this time.

The cases in which the yield of hydrogen gas was high also exhibited a material imbalance in hydrogen indicating that important net reactions other than those initially assumed, i.e. (1), (2), and (3) had come into play. The function of iron surfaces as "cracking" catalysts for benzene

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\* These results led to the earlier statement (p. 20) that it was not a surface effect but a phase difference which was responsible for the two-fold increase in benzene formation, in spite of a four-fold increase in surface area during vapor phase pyrolysis.

and other aromatic compounds is well known<sup>(14)</sup>. Hence, the surfaces of these metallic "wools" were examined after pyrolysis by X-ray and electron diffraction techniques for the presence of iron carbides. The results in each instance were negative. It is possible, however, that the amount of carbon being sought was too small to be detected by these techniques. Another possible explanation for this apparent excess of experimentally determined hydrogen is the formation of polyphenyls of higher molecular weight than quaterphenyl, accompanied by the release of hydrogen. These compounds were not detected, even though the column was operated occasionally at a temperature high enough to elute these polyphenyls<sup>(12)</sup>. Higher column temperatures were not utilized due to the possibility of decomposing the polyphenyl compounds.

For those experiments in which iron surfaces were present, the moles of biphenyl pyrolyzed were calculated by considering this additional net reaction:



The difference between the hydrogen yields in the material balance column (Table 6) divided by five was considered to be the amount of biphenyl decomposed by reaction (4). This amount of biphenyl was added to the amount decomposed by reactions (1), (2), and (3).

#### Views on the Decomposition Mechanism

The high-temperature thermal decomposition of organic compounds of many types, including hydrocarbons, is considered to proceed by chain mechanisms involving free radicals. From the literature<sup>(6,7)</sup> and from the present work there is no evidence that the decomposition of biphenyl is at variance with this, although conclusive statements concerning the

details of the mechanism cannot yet be made. A number of potentially useful considerations and experimental approaches were used to provide information which bears on the mechanism of biphenyl decomposition.

#### Initial Reaction Products

A primary purpose of the present research was the collection and identification of the initial products of the reaction. Accordingly, the extent of the biphenyl decomposition was kept below 1.5% in all of the experiments, and great care was taken to collect and identify the reaction products. As indicated by the results in Table 4, the principal products were benzene, terphenyls, and quaterphenyls and these were found in the approximate mole ratio of 4:2.5:1. Higher molecular weight products, if present, were below the limits of detection. Hydrogen gas was a product, but in amounts, on a molar basis, which were of the order of 5% or less of the benzene; the amounts of the individual low molecular weight hydrocarbons which were detected were, at the most, one-tenth of the hydrogen yield. Detailed analyses of the products were also reported by Kuper<sup>(7)</sup> and Gaumann and Rayroux<sup>(6)</sup>. The mole ratio for benzene, terphenyls, and quaterphenyls calculated from Kuper's results is 6:3.5:1, showing more benzene and terphenyls and/or less quaterphenyls than was obtained in the present work. The experimental details reported by Kuper, such as the weight of biphenyl and the size of the ampoules, indicate that a substantial fraction of the material in some experiments might have been in the vapor phase at the reaction temperature, whereas we kept the vapor volume to a minimum, as indicated on p. 20. Kuper also suggested that better temperature control would have been helpful in his experimentation. Furthermore, no data were reported on the yields of hydrogen or

other gases. Ampoule pretreatment, which we have found to be a significant factor in obtaining reproducible results, was not mentioned. The present results are in better agreement with those of Gaumann and Rayroux<sup>(6)</sup>. Consequently, we believe that the data which were obtained in the present research are valid for the thermal decomposition of pure biphenyl in the liquid phase.

Since the yields of benzene were large, it seems reasonable to assume that one initial step in the mechanism of decomposition is the formation of a pair of phenyl radicals:



These phenyl radicals could be converted either to benzene by the abstraction of hydrogen or to substituted cyclohexadienyl radicals ( $\text{C}_{18}\text{H}_{14}\text{H}\cdot$ ) by addition to biphenyl.<sup>(15)</sup>

Another initial step in the decomposition might be the reaction between two biphenyl molecules:



to form a biphenylyl radical and a substituted cyclohexadienyl radical. This reaction is, in effect, the dissociation of a C-H bond in biphenyl. Scavenging of the biphenylyl radicals by biphenyl molecules would lead to the formation of even higher molecular weight substituted cyclohexadienyl radicals. The various molecular species identified in the product mixture appear to be formed from the radicals by two paths: (1) the abstraction of hydrogen from neighboring species or (2) the disproportionation of the radical into product molecule and smaller free radical. The latter path may explain the formation of molecular hydrogen, which otherwise must be explained by radical-radical reactions or bimolecular reactions.

Analysis of the terphenyl isomers revealed that they were mostly meta and para oriented while the ortho form was almost entirely absent, even though the method of product separation was modified to prevent loss of the more volatile ortho isomer. The predominance of meta and para isomers is consistent with the belief that attack by phenyl radicals occurs more readily at exposed positions of the biphenyl molecules; the ortho position is shielded by the adjacent phenyl group. Furthermore, since the meta and para isomers were found in approximately equal amounts and the number of meta positions in biphenyl is twice the number of para positions, it appears that the para position has twice the reactivity of the meta positions. The orientations of the quaterphenyl isomers were found to be mainly meta-meta and meta-para, and such orientations are also reasonable.

Kuper<sup>(7)</sup> reported polyphenyl products of higher molecular weight than quaterphenyl only after the biphenyl decomposition had exceeded 20% at 426°C. Data from engineering tests of organic coolants indicate that the average molecular weight of the polyphenyl products increased with time. From this, it seems reasonable to assume that the radicals formed by primary processes add to product molecules at rates which are functions of the product concentrations. These reactions result in a gradual increase in the average molecular weight of the product mixture.

#### Thermochemistry and Bond Energies

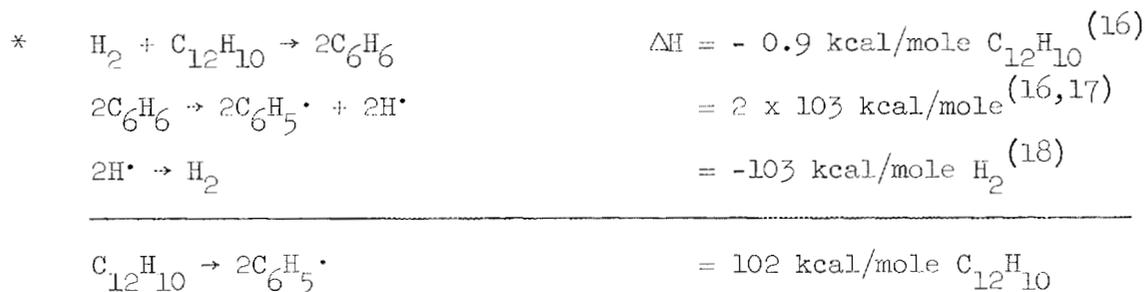
A plausible mechanism for the decomposition reaction must meet the energy requirements of the processes taking place. The three distinct types of bonds to be found in biphenyl are the C-H bond, the C-C bond

between phenyl groups, and the C=C bond within the ring structure. The bond dissociation energy for C<sub>6</sub>H<sub>5</sub>-H is about 103 kcal/mole<sup>(16,17)</sup>, and we assume, as did Gaumann and Rayroux<sup>(6)</sup>, that little difference exists between the strength of this bond in benzene and in biphenyl. The energy necessary for:



is calculated to be about 102 kcal<sup>\*</sup>, nearly identical with that for C-H bond rupture. Therefore, the probability of having one of these bonds break to the exclusion of the other cannot be great. The relatively high dissociation bond energy of 124 kcal/mole<sup>(19)</sup> for C=C bonds in the ring accounts for the formation of only small amounts of the low molecular weight hydrocarbons which were found.

Since our observed activation energy for biphenyl decomposition is only 62 kcal/mole, considerably lower than the C-C and C-H bond energies, further support is thereby provided for the suggestion that a chain mechanism involving free radicals is the principal decomposition path. This implies that steps of low activation energy for radical regeneration are involved, but these steps have not yet been identified.



### Rate Studies

It was not a purpose of this investigation to determine the rate of biphenyl decomposition over a wide range of percentage decomposition. The pyrolysis of the biphenyl was so limited that no effective change in the amount of biphenyl was achieved. Other workers<sup>(4, 7)</sup> have reported that the decomposition is first order with respect to biphenyl. Therefore, our data are presented in this form in Fig. 10. With the small extent of decomposition, it is impossible for our data to confirm or deny a first order rate law. Indeed, linear plots of yields of products versus time were used in order to find the rates given in Table 5.

### Tracer Study

A deliberate addition of deuterium gas, equal in amount to the hydrogen gas normally produced, to biphenyl was made prior to pyrolysis for 12 hours at 422°C. This was done to test the hypothesis advanced by Kuper<sup>(7)</sup> that hydrogen molecules react with an activated complex to form benzene. Subsequent mass spectrometric analysis failed to reveal the presence of any benzene enriched in deuterium. Hence, it appears that molecular hydrogen does not play an important role in the formation of benzene during the thermal decomposition of biphenyl.

Furthermore, Sykes<sup>(20)</sup> points out that there is negative evidence for the formation of free hydrogen atoms during the course of reaction between aryl radicals and aromatic molecules. It seems more likely that the hydrogen is abstracted by other radicals or molecules as suggested in the last section. The mechanism presented by Gaumann and Rayroux<sup>(6)</sup> for biphenyl decomposition is not consistent with this view.

Effect of Added Substances

The decomposition mechanism appears to be obscured by the presence of oxygen or catalytically active surfaces during pyrolysis. The addition of 0.1 mole % oxygen caused the production of large quantities of carbon monoxide, doubled the yields of hydrogen, benzene, and terphenyl, and gave a five-fold increase in the yield of quaterphenyl. The material balance for the reaction (see Table 4) was also upset. In early experiments, before the pretreatment of ampoules was adopted, large amounts of carbon monoxide were obtained along with erratic yields of benzene. It is believed that oxygen released from the glass was responsible for these early results. Both iron wool and stainless steel wool, catalytically active surfaces for hydrocarbons, increased the yield of hydrogen by a factor of 10. The function of inert surfaces in radical chain reactions is frequently one of chain breaking through radical recombination at the surface. This may account for the significant reduction of the benzene yield in the presence of either Pyrex wool or quartz wool. The addition of a small amount of water before pyrolysis did not appear to affect the course of the decomposition reaction, although it is known to be important in the presence of radiation.

Unfortunately, it is not possible to present a complete mechanism for the thermal decomposition of biphenyl. A better understanding of the energy relationships and of the reaction rates for the individual steps in the reaction sequence would allow more accurate estimation of the probabilities of the suggested reaction paths. A study of the reactivities of the various aromatic hydrocarbons toward free radicals, generated by methods other than high temperature, would assist in deciding

the relative contribution of probable radical reactions. For instance, the reaction of biphenyl with phenyl radicals from benzoyl peroxide at temperatures below pyrolysis temperatures might shed light on the relative importance of phenyl and biphenylyl reactions in product formation. Similarly, pyrolyses of biphenyl in the presence of  $C^{14}$  labelled compounds would help in selection of the reaction sequences leading to specific products. Also, the use of such tracer experiments could yield information of the reversibility of the suggested reactions. As an example, the isotopic distribution of deuterium in biphenyl after pyrolysis of biphenyl containing added deuterobiphenyl would show whether or not scrambling occurs due to hydrogen transfer between biphenylyl radical and biphenyl.

Information of this nature would aid greatly in establishing a unique mechanism for the decomposition.

#### 4. ACKNOWLEDGEMENT

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## VI. Appendix A. Yield of Major Products from Biphenyl Pyrolysis

 (2.86 x 10<sup>-2</sup> moles  $\phi_2$ )

Temp. (°C)	Time (hr)	H <sub>2</sub> (moles)	CH <sub>4</sub> (moles)	CO (moles)	$\phi$ H (moles)	o- $\phi_3$ (moles)	m- $\phi_3$ (moles)	p- $\phi_3$ (moles)	* $\phi_4$ (moles)	* $\phi_4$ ' (moles)	m- $\phi_4$ (moles)	m,p- $\phi_4$ (moles)	p- $\phi_4$ (moles)
		x 10 <sup>-6</sup>	x 10 <sup>-7</sup>	x 10 <sup>-7</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-6</sup>	x 10 <sup>-6</sup>	x 10 <sup>-6</sup>	x 10 <sup>-6</sup>	x 10 <sup>-6</sup>
422	12	2.2	0.8	4.8	3.7	0.00	1.53	0.98	0.9	0.46	2.8	2.2	0.00
		2.9	1.4	6.6	4.8	0.00	1.91	1.46	1.1	0.46	5.1	3.4	0.00
		2.1	1.0	6.0	3.6	0.00	1.43	1.24	1.2	0.46	5.5	2.2	0.00
Average		2.4	1.1	5.8	4.0	0.00	1.62	1.23	1.1	0.46	4.5	2.8	0.00
	24	3.8	1.6	2.2	7.3	0.35	3.34	1.73	2.3	0.98	5.0	3.6	0.07
		3.9	1.6	2.2	7.8	0.35	2.53	1.70	2.2	1.3	5.4	3.9	0.00
		3.7	1.2	1.6	6.5	0.30	3.26	1.79	2.5	1.3	5.3	3.6	0.00
Average		3.8	1.5	2.0	7.2	0.33	3.04	1.74	2.3	1.2	5.2	3.7	0.02
	48	7.6**	6.3	ca 15	15.4**	0.73	5.1	3.3	6.0	3.7	12.6	11.2	1.6
438	8	4.8	2.3	9.0	6.0	0.30	2.72	1.60	2.2	1.7	5.2	5.5	1.0
		4.7	1.6	8.0	7.1	0.26	2.76	1.89	2.1	1.4	5.5	5.5	0.6
		4.7	1.6	9.0	6.9	0.16	2.68	1.98	2.4	1.7	6.0	6.1	0.9
Average		4.7	1.8	8.7	6.7	0.24	2.72	1.82	2.2	1.6	5.6	5.7	0.8
	12	7.2	2.9	10.2	10.5	0.63	3.39	2.66	5.1	2.4	10.2	9.0	1.1
		6.6	1.1	1.9	11.3	0.69	3.88	2.90	5.4	2.7	11.3	10.2	1.5
		7.3	2.9	6.4	11.2	0.62	3.62	2.86	4.9	2.7	11.0	10.2	1.3
Average		7.0	2.3	6.2	11.0	0.65	3.63	2.81	5.1	2.6	10.8	9.8	1.3
	16	8.0	4.8	11.0	15.4	-	4.74	3.76	4.6	2.5	12.6	11.4	1.4
		7.2	2.8	8.2	13.6	0.87	4.86	3.57	4.9	2.6	11.7	10.6	1.4
		7.2	2.8	8.4	13.4	0.76	4.31	3.37	3.5	2.2	11.8	10.8	1.2
		8.5	2.4	7.6	14.8	0.76	4.74	3.53	5.7	2.9	12.9	12.8	-
Average		7.7	3.2	8.8	14.3	0.80	4.67	3.56	4.7	2.6	12.3	11.4	1.3

\* Unidentified products.

\*\* Confirmed by earlier experiments for which there are no polyphenyl results.

## Appendix A, continued

Temp. (°C)	Time (hr)	H <sub>2</sub> (moles)	CH <sub>4</sub> (moles)	CO (moles)	φH (moles)	o-φ <sub>3</sub> (moles)	m-φ <sub>3</sub> (moles)	p-φ <sub>3</sub> (moles)	*φ <sub>4</sub> (moles)	*φ <sub>4</sub> ' (moles)	m-φ <sub>4</sub> (moles)	m,p-φ <sub>4</sub> (moles)	p-φ <sub>4</sub> (moles)
		x 10 <sup>-6</sup>	x 10 <sup>-7</sup>	x 10 <sup>-7</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-5</sup>	x 10 <sup>-6</sup>	x 10 <sup>-6</sup>	x 10 <sup>-6</sup>	x 10 <sup>-6</sup>	x 10 <sup>-6</sup>
446	8	5.9	1.7	2.0	10.1	0.21	3.46	2.21	3.4	1.9	8.7	8.8	1.6
		6.2	1.6	2.0	10.5	-	3.58	2.42	3.6	2.1	9.5	9.9	1.9
		6.3	1.2	1.8	10.6	0.20	3.66	2.37	3.8	2.3	9.2	9.7	1.7
Average		6.1	1.5	1.9	10.4	0.21	3.57	2.33	3.6	2.1	9.1	9.5	1.7
	12	10.2	3.1	4.0	17.6	0.91	4.92	4.03	8.0	4.4	16.7	15.9	2.7
		9.1	1.7	2.0	16.9	0.83	4.70	4.07	7.9	4.4	16.6	15.5	2.5
		9.2	1.8	2.0	15.9	0.93	4.79	4.03	8.0	4.5	16.9	15.4	2.4
Average		9.5	2.2	2.7	16.8	0.89	4.80	4.04	8.0	4.4	16.7	15.6	2.5
<u>5 x 10<sup>-4</sup> moles H<sub>2</sub>O added</u>													
422	12	2.1	1.0	1.2	3.2	0.00	2.02	1.35	1.5	1.1	3.1	-	-
		2.2	0.6	1.5	3.0	0.11	1.82	1.28	1.1	1.0	2.3	2.3	0.20
		2.0	0.4	1.0	3.1	0.11	1.72	1.03	1.1	0.9	2.3	1.9	0.20
		1.9	1.0	1.2	3.0	0.00	-	-	-	-	2.7	2.0	0.23
Average		2.1	0.8	1.2	3.1	0.06	1.85	1.21	1.2	1.0	2.6	2.1	0.21
<u>2 x 10<sup>-5</sup> moles O<sub>2</sub> added</u>													
422	12	5.2	3.0	ca 60	8.0	0.31	2.92	2.00	9.5	6.2	15.1	15.2	2.5
		5.1	2.6	ca 50	7.1	0.41	3.09	2.19	8.8	5.7	14.5	15.1	3.2
		5.3	2.8	ca 65	7.4	0.43	2.82	1.83	8.7	5.4	14.9	16.0	3.0
		4.6	2.8	ca 65	6.4	0.37	2.80	1.81	8.1	5.1	14.1	14.7	2.8
Average		5.1	2.8	ca 60	7.2	0.38	2.91	1.96	8.8	5.6	14.7	15.3	2.9

\* Unidentified products.

Appendix B. Yield of Major Products from Biphenyl Pyrolysis in Presence of Added Surfaces

(Conditions: 500 cm<sup>2</sup>, 12 hrs, 422°C, 1.95 x 10<sup>-2</sup> moles  $\phi_2$ )

Surface	H <sub>2</sub> (moles) x 10 <sup>-6</sup>	CH <sub>4</sub> (moles) x 10 <sup>-7</sup>	CO (moles) x 10 <sup>-7</sup>	$\phi$ H (moles) x 10 <sup>-5</sup>	o- $\phi_3$ (moles) x 10 <sup>-5</sup>	m- $\phi_3$ (moles) x 10 <sup>-5</sup>	p- $\phi_3$ (moles) x 10 <sup>-5</sup>	*Q' <sub>4</sub> (moles) x 10 <sup>-6</sup>	*Q'' <sub>4</sub> (moles) x 10 <sup>-6</sup>	m- $\phi_4$ (moles) x 10 <sup>-6</sup>	m,p- $\phi_4$ (moles) x 10 <sup>-6</sup>	p- $\phi_4$ (moles) x 10 <sup>-6</sup>
Pyrex	3.0	4.0	7.0	1.6	0.08	0.70	0.53	0.65	0.26	1.3	1.2	0.00
Quartz	1.4	1.0	4.4	2.0	0.07	0.69	0.55	0.59	0.26	1.4	1.1	0.00
Iron	ca 12	ca 20	ca 10	2.3	0.10	1.10	0.86	0.82	0.33	2.0	2.0	0.00
Stainless steel	13.8	17.4	1.0	1.3	0.00	0.74	0.30	0.16	0.36	0.75	0.29	0.00
Quartz + SS (1:1)	16.0	22.8	32.2	1.8	0.00	0.75	0.60	0.65	0.39	1.5	1.4	0.00

\* Unidentified products.

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