325/

2-26-65

NAA-SR-8277

COPY

MASTER

RADIOLYTIC AND PYROLYTIC DECOMPOSITION OF ORTHO TERPHENYL AT HIGH TEMPERATURE

AEC Research and Development Report

PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

DISCLAIMER

DISCLAIMER

NAA-SR-8277
CHEMISTRY
28 PAGES

RADIOLYTIC AND PYROLYTIC DECOMPOSITION OF ORTHO TERPHENYL AT HIGH TEMPERATURE

By
J.M. SCARBOROUGH

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED:

DISTRIBUTION

This report has been distributed according to the category "Chemistry" as given in "Standard Distribution Lists for Unclassified Scientific and Technical Reports," TID 4500 (31st Ed.), June 1, 1964. A total of 635 copies was printed.

ACKNOWLEDGMENT

The author wishes to express his appreciation to G. Billings, II for the able assistance he provided in all phases of the laboratory work and to H. H. Neely, T. D. Hogan, and J. C. Robinson for the excellent irradiation services they provided.

CONTENTS

TABLES

FIGURES

ABSTRACT

The pyrolytic decomposition rates of ortho-terphenyl were determined at various temperatures between 750 and 900°F and the temperature dependence of the initial rates established. The formation rates for biphenyl in the pyrolysis of ortho-terphenyl were also determined.

The radiolytic decomposition of ortho-terphenyl was studied in the same temperature range using 1.0 Mev electrons from a Van de Graaff generator. The temperature dependence of initial radiolytic decomposition rates was established. Comparisons were made between the pyrolytic and radiolytic behavior of ortho-terphenyl.

I. INTRODUCTION

In order to evaluate the highest feasible temperature at which organic cooled reactors may be operated, knowledge of the radiolytic and pyrolytic behavior of terphenyls at temperatures above 750°F is required. Although some isolated experiments have been reported at these temperatures,[1,2,3,4] systematic behavioral studies of the terphenyls have not been made previously.

To supply these data, a program was established to study the radiolytic and pyrolytic behavior of the polyphenyls above 750°F. The effects of temperature, composition, linear energy transfer (LET), dosage rates, and container materials were to be studied systematically in such a way that the variables could be evaluated individually or in combination. This report covers the work completed prior to October 1962, at which time the project was terminated.

II. PYROLYSIS OF ORTHO-TERPHENYL

Information on pyrolysis is important as a basis for the comparison of radiolytic and pyrolytic behavior. Such information is also valuable to reactor designers for estimating damage to coolant outside a reactor core.

Although mixtures of the terphenyl isomers are most likely to be used as reactor coolants, pure ortho-terphenyl was selected for the initial investigation because it is the least stable of the terphenyl isomers. The use of a pure isomer also allows advantages in sample purification, analysis, and interpretation of experimental results.

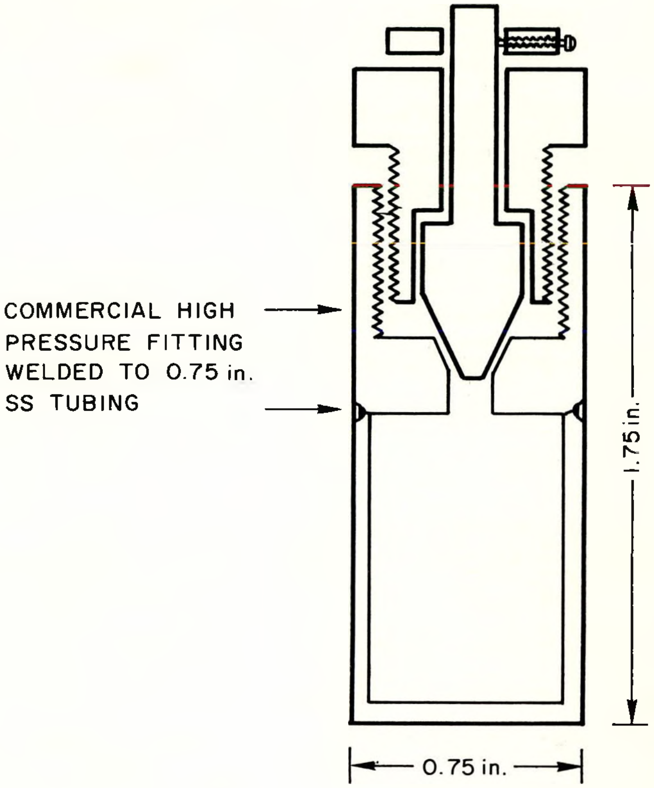
A. EXPERIMENTAL TECHNIQUES

A large supply of ortho-terphenyl was prepared in order to provide identical samples for both the pyrolysis and radiolysis experiments. About 2 kg of material was prepared by combining and thoroughly mixing 100-gm lots of Eastman White label grade ortho-terphenyl. Further purification of this material proved to be unnecessary since no impurities could be found by vapor phase chromatography.

Capsules for the pyrolysis experiments were made of type 304 stainless steel fitted with a standard "gland and plug" high pressure fitting. A drawing of the capsule is shown in Figure 1. A special device was designed in which the sample could be degassed and sealed under vacuum.

Pyrolysis experiments were carried out by heating capsules of ortho-terphenyl in which the temperature was controlled to ±6°F by means of a Wheelco Recorder controller in conjunction with a magnetic amplifier and saturable core reactor. Temperature of the individual capsules was monitored by means of thermocouples attached to the outside walls of the capsules. Preliminary measurements, using special capsules in which thermocouples inside the capsules were in contact with the ortho-terphenyl, showed that the temperature of the terphenyl was essentially identical to that of the outside wall of the capsule. Only during initial heating to reach the experimental temperature was there a barely perceptible lag between the coolant temperature and the outside wall temperature.

In order to prevent excessive damage to the sample before the experimental temperatures were attained in the experiments at 900°F (and to improve temperature control), the capsules were preheated to 750°F in an auxilliary furnace and quickly inserted into the furnace controlled at 900°F.



6-29-64 7500-1527

Figure 1. Pyrolysis Capsule

Samples were prepared for pyrolysis in the following manner. Approximately 2 gm of ortho-terphenyl was transferred from a storage flask maintained at 80 to 90°C (protected by a nitrogen atmosphere) to a clean, weighed capsule by means of a hypodermic syringe. The capsule was sealed and placed in a vacuum system and outgassed by the freeze-melt technique. When pumping produced no additional gas, the capsule was sealed at less than 10^{-4} mm Hg, removed from the vacuum system, and weighed to determine the exact amount of terphenyl.

The capsules were then heated at the selected temperature for a carefully measured time, removed from the furnace, and analyzed. Control samples were run at each temperature in order to determine the amount of decomposition during the initial heating period and during the cooling period following removal from the furnace. Thus, the net damage at the experimental temperature could be determined.

The entire sample was removed from the capsule and dissolved in benzene for chromatographic analysis in order to minimize sampling errors.

Samples were analyzed by gas chromatography using a Loenco Model 15A gas chromatograph, utilizing columns of apiezon on firebrick at constant temperature of 300°C. Some of the analyses to determine impurities in the stock material were performed on a Loenco Model 17 chromatograph with temperature programming, utilizing a combustion technique for increased sensitivity.[5,6]

Experimental results for the pyrolysis experiments are shown in Table 1. The concentration (weight-fraction) of ortho-terphenyl remaining as a function of time at a given temperature was found to be best represented by a first order equation of the form,

$$(1 - y) = e^{-kt}, \qquad \ldots(1)$$

where (1 - y) is the fraction of ortho-terphenyl remaining after t hours and k is a specific rate constant (initial decomposition rate). The expression for the differential decomposition rate (reaction velocity) is therefore of the form,

$$-\frac{d(1 - y)}{dt} = \frac{dy}{dt} = k e^{-kt} = k(1 - y). \qquad \ldots(2)$$

The specific reaction rate, k, for each temperature was derived by fitting the data to the above first order expression by the method of least squares. Thus, the specific reaction rates in weight-fraction decomposed per hour at 786, 802, 851, and 900°F were 0.00067, 0.00154, 0.0103, and 0.0588, respectively. Figure 2 shows the semi-log plots of concentration vs time in hours.

The initial thermal decomposition rate (specific reaction rate) for ortho-terphenyl as a function of temperature is given by the expression,

$$\ln R_{(-\phi_3)} = -\frac{36099}{T} + 44.9803, \qquad \ldots(3)$$

where R is in weight fraction per hour and T is the temperature in degrees Kelvin. (Note: Rate, R, is good only to 2 or 3 significant figures. More figures are carried in the logarithmic equation for convenience. The treatment is similar throughout the report.) An Arrhenius plot of specific rate constants is shown in Figure 3; the corresponding activation energy is 71.7 ± 1.3 kcal/mole.

The data for biphenyl formation shown in Table 1 were taken from chromatograms obtained specifically for the determination of ortho-terphenyl. Consequently the chromatographic conditions were not ideal for the determination of biphenyl and the resultant data are scattered. Due to this scatter it is not possible to establish clearly whether biphenyl formation is a zero or first order reaction.

TABLE 1

PYROLYSIS OF ORTHO-TERPHENYL

Temperature (°F)	Time (hr)	Composition of Sample (Weight Fraction)		
		Ortho-Terphenyl $(1 - y)$	Total Decomposition Products (y)	Biphenyl (ϕ_2)
786 ± 10	31	0.976	0.024	—
	99	0.941	0.059	—
	135	0.912	0.088	—
	216	0.868	0.132	—
	272	0.831	0.169	—
802 ± 5	30	0.955	0.045	0.0106
	72	0.900	0.100	0.0260
	80	0.880	0.120	—
	112	0.847	0.153	0.0394
	160	0.776	0.224	0.0626
	162	0.787	0.213	—
851 ± 5	10	0.899	0.101	0.0267
	20	0.825	0.175	0.0477
	30	0.749	0.251	0.0662
	60	0.531	0.469	0.1284
	81	0.424	0.576	0.1567
900 ± 5	0.5	0.978	0.022	0.0083
	1.0	0.947	0.053	0.0134
	1.5	0.913	0.087	0.0216
	2.3	0.860	0.140	0.0329
	3.0	0.848	0.152	0.0411
	4.0	0.790	0.210	0.0550

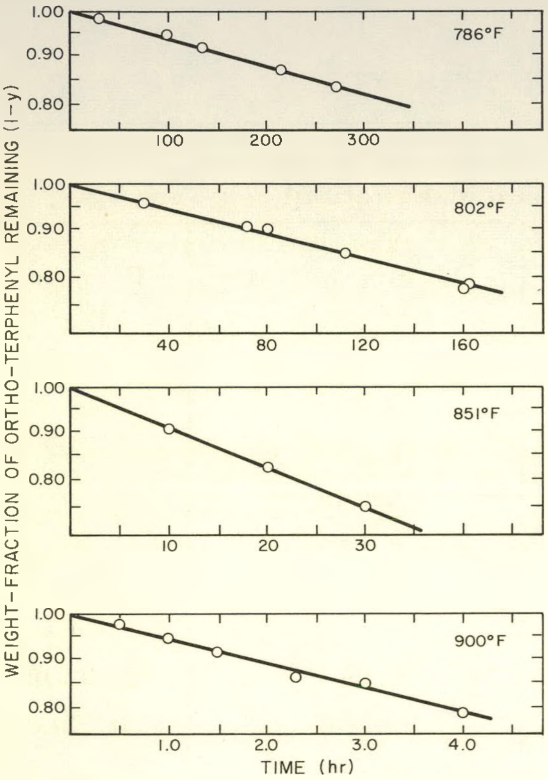
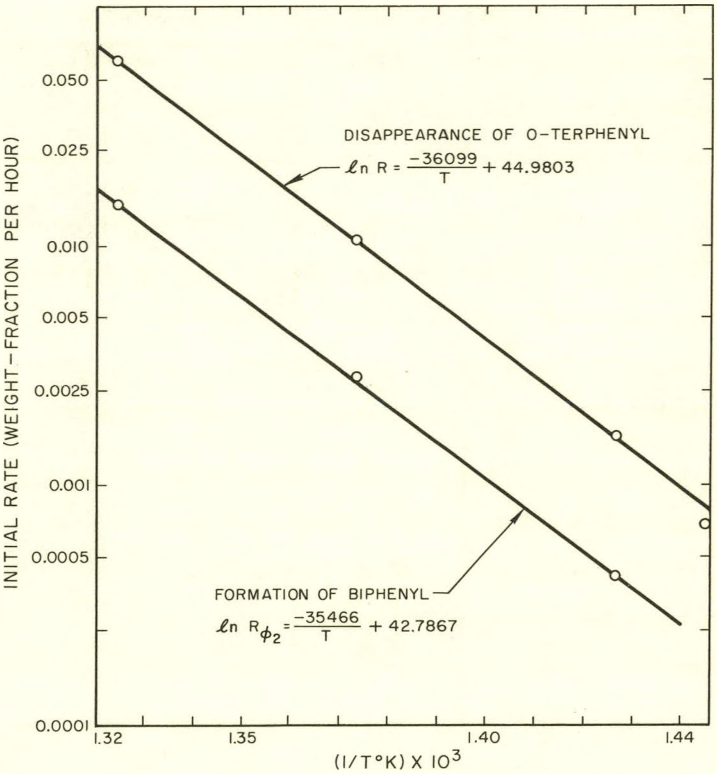


Figure 2. Pyrolysis of Ortho-Terphenyl

6-29-64 7500-1528

Figure 3. Terphenyl Disappearance — Biphenyl Formation



6-29-64 7500-1529

However, the data fit a first order equation of the form,

$$\phi_2 = c(1 - e^{-kt}), \qquad \ldots(4)$$

somewhat better. The weight fraction of biphenyl present at time, t (hr), is represented by ϕ_2, k is the specific rate constant for terphenyl disappearance, and c is a constant. At 802, 851, and 898°F, the initial formation rates (c x k) in weight fraction per hour, for biphenyl are 0.00040, 0.0028, and 0.0149, respectively. The rates are essentially the same if zero order is assumed.

The temperature dependence of biphenyl formation is given by the expression,

$$\ln R_{(\phi_2)} = -\frac{35466}{T} + 42.7867, \qquad \ldots(5)$$

where R is in weight-fraction per hour and T is in °K, which corresponds to an activation energy of 70.5 ± 3.8 kcal/mole.

B. DISCUSSION OF RESULTS

The primary thermal decomposition of the ortho-terphenyl molecule may be expected to occur mainly through the rupture of the interannular C-C bonds to form phenyl and biphenyl radicals. Decomposition is the net result of the reaction of these primary radicals with the substrate.

The most probable fate of the primary phenyl and biphenyl radicals is the addition to the terphenyl substrate molecules to form larger radicals.[7] These radicals can add to other substrate molecules or can dissociate to form smaller radicals and neutral molecules. Such processes continue until the radical chains are terminated. Biphenyl is probably formed by one of these dissociation reactions.

The fact that the observed activation energy for terphenyl disappearance is identical within experimental error to that for the formation of biphenyl and that both processes follow apparent first order kinetics suggests that the steps leading to both processes have the same rate controlling step. Product forming steps are therefore believed to be fast compared to the primary dissociation of terphenyl.

Although there are insufficient data in the literature on the pyrolytic decomposition of ortho-terphenyl for comparison to this work, it may be noted that the activation energy for the thermal decomposition of the other terphenyl isomers and mixtures has been reported to be about 70 kcal/mole.[2,3,4]

III. RADIOLYSIS OF ORTHO-TERPHENYL

The radiolysis of polyphenyl organic coolant materials has been the subject of many investigations;[1,4,8,9,10,11] however, as in the study of the pyrolytic decomposition of the polyphenyls, very little work has been done at temperatures exceeding 750°F. Neither has there been a systematic study of the parameters, temperature, composition, total dosage, dosage rate, LET, and catalytic surfaces; but, rather, independent studies of one or two of the parameters without regard to the others.

A systematic investigation of the radiolytic and pyrolytic behavior of polyphenyl coolants was initiated which would take cognizance of the importance of the parameters listed above. One of the early goals of this program was to obtain data on the radiolytic decomposition of the polyphenyls at temperatures above 750°F in order to establish maximum, feasible operating temperatures for organic cooled reactors.

The data on the radiolytic decomposition of ortho-terphenyl at high temperature obtained through October 1962, when the project was cancelled due to curtailment of the organic reactor program, are presented in this section.

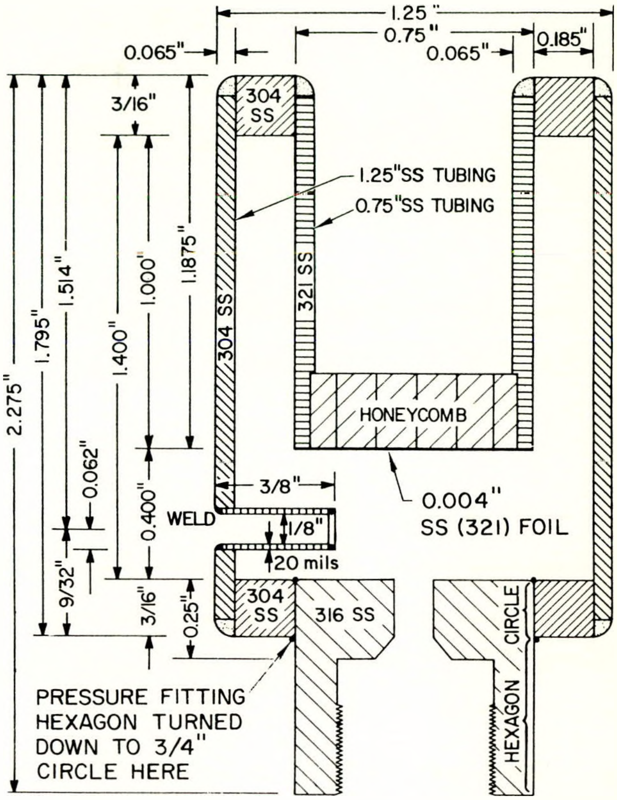
A. EXPERIMENTAL TECHNIQUES

The ortho-terphenyl used in the radiolysis experiments was the same as that used for the pyrolysis experiments (cf Part II).

Capsules for the radiolysis experiments were designed and fabricated to withstand temperatures in excess of 900°F and pressures as high as 700 psi with adequate margins of safety. The design also allowed the capsules to be easily opened and closed under vacuum, and provided an irradiation window thin enough to permit the passage of electrons. Figure 4 shows a drawing of the irradiation capsules. Tests showed that capsules of this design did not rupture at a pressure of 1600 psi at 900°F in air.

Special heaters and temperature controllers were required to give high heating rates as well as good control. The furnace assembly was fabricated by silver soldering a heater element (made from nichrome wire sheathed in MgO and stainless steel) to a thin stainless steel sheath that slipped snugly over the capsules. The control system utilized a recorder-controller which drove a magnetic amplifier which regulated the power to the heater circuit via a saturable core reactor.

Experimental procedure in the radiolysis experiments was essentially the same as that in the pyrolysis experiments. The clean weighed capsules were filled with enough ortho-terphenyl to ensure complete submersion of the electron window during irradiation. The transfer of liquid ortho-terphenyl was performed in a nitrogen atmosphere. The samples were degassed by the standard freeze-melt technique and were sealed at less than 10^{-4} mm Hg. The sealed capsule was weighed in order to determine the weight of the sample.



6-29-64 7500-1530

Figure 4. High Pressure Irradiation Capsule

The capsule and heater were positioned on the Van De Graaff generator and preheated to approximately 750°F. The temperature controller was allowed to take over just prior to the start of irradiation. The electron beam was turned on as soon as the sample reached the control temperature (approximately 3 min). Beam energy was maintained at 1.00 ± 0.01 Mev (98% of the electrons) and the beam current (30 to 35 μa) was adjusted to give a dosage rate of approximately 0.8 watt/gm of sample. When the irradiation was completed, the sample was handled in essentially the same manner as the pyrolysis samples, except that a fraction of the total sample was analyzed. The sample was melted, mixed thoroughly, and 2-gm portions were removed by syringe for analysis.

Samples of ortho-terphenyl were irradiated to various total dosages at 750, 802, 850, and 898°F. The experimental results are shown in Table 2.

Prior to the irradiation of terphenyl samples, dosimetry measurements were made utilizing the hydrogen yields from benzene.[8,13,14,15] The benzene samples were treated in the same manner as terphenyl samples except that the

TABLE 2

RADIOLYSIS OF ORTHO-TERPHENYL

Temperature (°F)	Time (hr)	Total Dosage (w - hr/gm)	Dosage Rate (w/gm)	Composition of Sample (Weight Fraction)		
				Ortho-Terphenyl (1 - y)	Total Decomposition Products (y)	Biphenyl (ϕ_2)
752 ± 6	0.517	0.419	0.810	0.923	0.077	0.0056
	1.00	0.862	0.862	0.900	0.100	0.0075
	1.58	1.296	0.820	0.862	0.138	0.0238
	3.00	2.473	0.824	0.789	0.211	0.0372
	4.08	3.342	0.819	0.749	0.251	0.0454
	5.0	4.438	0.888	0.696	0.304	0.0557
	12.0	9.91	0.826	0.589	0.411	0.0678
	20.0	16.45	0.823	0.477	0.523	0.756
802 ± 6	0.333	0.241	0.723	0.931	0.069	0.0178
	0.750	0.541	0.721	0.866	0.134	0.0348
	1.25	0.940	0.752	0.827	0.173	0.0405
	1.50	1.071	0.714	0.823	0.177	0.0389
	3.00	2.140	0.713	0.709	0.291	0.0649
	6.75	4.766	0.706	0.568	0.432	0.0856
	10.0	7.170	0.717	0.447	0.553	0.103
850 ± 6	0.50	0.431	0.861	0.815	0.185	0.0448
	0.80	0.689	0.861	0.760	0.240	0.0585
	1.53	1.310	0.856	0.673	0.327	0.0805
898 ± 6	0.50	0.445	0.889	0.752	0.248	0.0639
	1.00	0.893	0.893	0.643	0.357	0.0904
	1.50	1.252	0.834	0.595	0.405	0.103
	2.3	1.830	0.796	0.500	0.500	0.123

benzene samples were maintained at 25 to 30° C in a stream of air. Eight capsules containing benzene were each irradiated to a total dosage (to the capsule) of 1.02×10^{24} ev and the hydrogen yield was determined. The energy absorbed by the benzene in the capsule was calculated from the hydrogen yield using a value of 0.038 for the $G(H_2)$ of benzene. It was found that the fraction of the electron beam energy which was absorbed by the benzene was 0.198 ± 0.005. Pertinent data are shown in Table 3.

TABLE 3

BENZENE DOSIMETRY*

Hydrogen Yield (cc STP)	Energy Absorbed By Sample† (ev)	Fraction of Beam Energy Absorbed By Sample
2.87	2.03×10^{23}	0.200
2.76	1.95×10^{23}	0.192
2.91	2.05×10^{23}	0.202
2.95	2.09×10^{23}	0.205
2.80	1.98×10^{23}	0.194
2.86	2.02×10^{23}	0.198
2.87	2.03×10^{23}	0.199
2.78	1.97×10^{23}	0.193
		0.198 ± 0.005§

*All benzene samples irradiated to total dosage of 1.02×10^{24} ev

†Based on G_{H_2} benzene = 0.038

§Average

B. TERPHENYL DISAPPEARANCE

Preliminary treatment of the data for terphenyl disappearance (Table 2) indicated that a complex relationship existed between terphenyl concentration and dosage. Terphenyl disappearance does not follow a simple first, second, or third order rate law.

Since simple first, second, or third order kinetic equations did not provide satisfactory representation of the data, the differential method[16] for determining the apparent reaction order and estimating initial rates was used to establish a relationship between terphenyl concentration and dosage.

This method is based on the fact that the rate of a reaction of the n^{th} power of the concentration of the reactant in question. If c is the concentration at any instant, where k is the specific rate constant and n the order, then,

$$-\frac{dc}{dt} = kc^n . \qquad \ldots(6)$$

Thus,

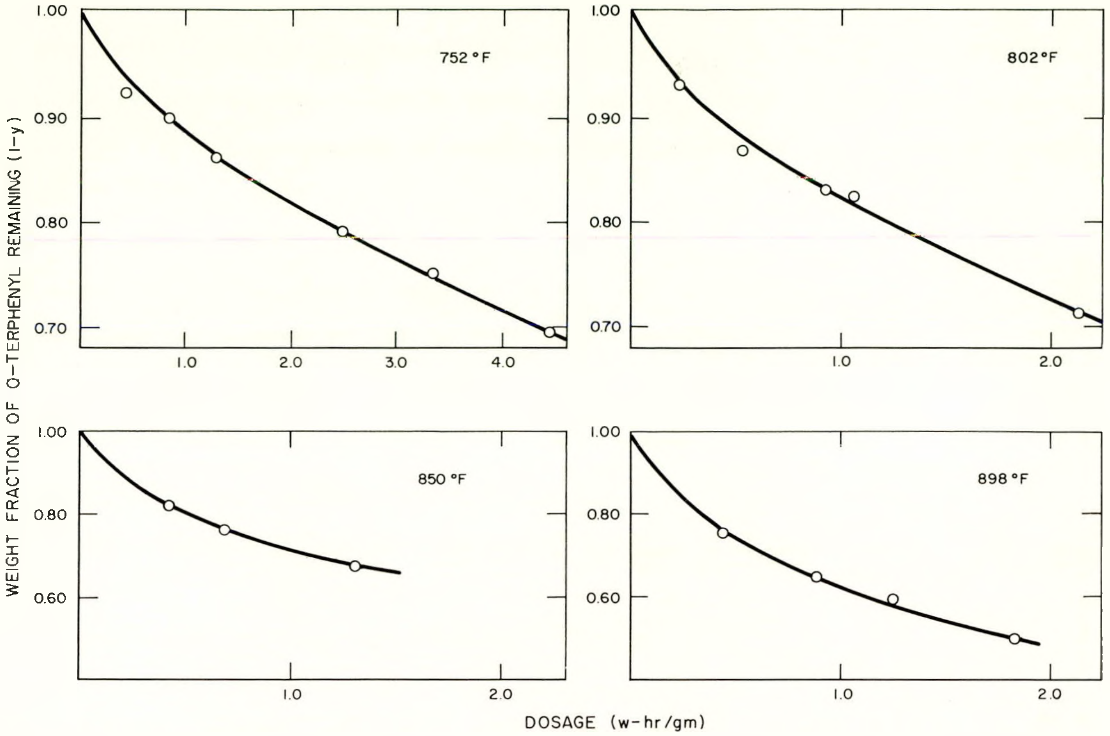
$$\ln(-dc/dt) = \ln k + n \ln c . \qquad \ldots(7)$$

If ln(-dc/dt) is plotted against ln c for a kinetically simple reaction a straight line of slope n (the order) is obtained. The intercept of the ordinate gives k, the initial decomposition rate. A curve of variable slope is obtained if the reaction has complicating features.

To utilize this method, the decomposition rate, -dc/dt, is required at several concentrations over an appreciable time period. Usually $\Delta c/\Delta t$ is measured and assumed to be -dc/dt, corresponding to the mean value of c in the interval considered.

In the treatment of the data for the radiolysis of ortho-terphenyl at higher temperature, the weight fraction (1 - y) of terphenyl remaining in the samples after irradiation was plotted against total dosage D, in watt-hours per gram (Figure 5). The slope of the curve, $\Delta(1 - y)/\Delta D$, was determined at various values of (1 - y) and these ratios were assumed to be equivalent to the instantaneous decomposition rate dy/dD (grams per watt-hour). These instantaneous decomposition rates for the various temperatures are shown in Table 4. Plots of ln(dy/dD) vs ln(1 - y) which were made for each set of irradiations are shown in Figure 6.

These curves indicate that the apparent order for the disappearance of ortho-terphenyl is high and variable. Fourth order kinetics appear to offer the



6-29-64 7500-1531

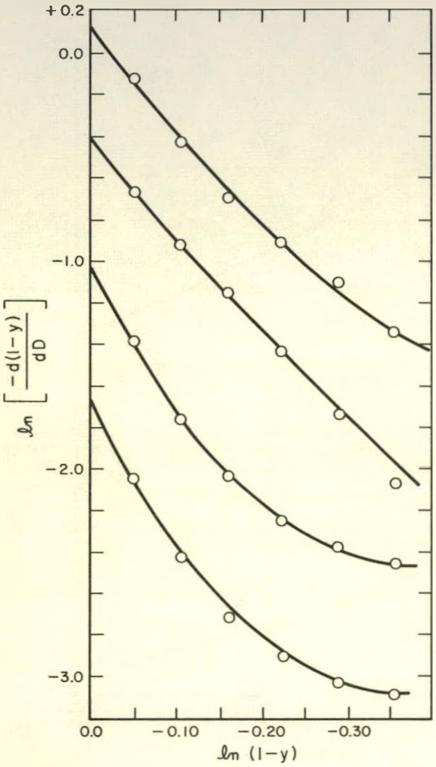
Figure 5. Radiolysis of Ortho-Terphenyl

TABLE 4

INSTANTANEOUS DECOMPOSITION RATES FOR ORTHO-TERPHENYL

(1 - y)		-d(1 - y)/dD*		
	752°F	802°F	850°F	898°F
1.00†	0.185	0.350	0.660	1.10
0.95	0.130	0.250	0.524	0.877
0.90	0.0885	0.172	0.398	0.649
0.85	0.0662	0.129	0.313	0.500
0.80	0.0546	0.105	0.237	0.403
0.75	0.0483	0.093	0.172	0.327
0.70	0.0460	0.087	0.124	0.261
0.65				0.208
0.60				0.168

*-d(1 - y)/dD = dy/dD, gm/w-hr
†Extrapolated initial rate



6-29-64 7500-1532

Figure 6. Decomposition Rate as a Function of Concentration

best "average" representation of the data. Rate constants calculated from the experimental data (Table 5) show that the graphical interpretation is valid in that fourth order rate constants provide the best fit of the data. Ortho-terphenyl is the major component of the reaction mixture and is involved in essentially all of the reactions subsequent to the primary dissociations; thus it is not surprising that the apparent order for ortho-terphenyl disappearance is high and variable.

Initial decomposition rates were also obtained from the curves shown in Figure 6 by extrapolating to zero decomposition. These rates are shown in Table 4 and the temperature dependence of these rates is shown in an Arrhenius plot in Figure 7. The temperature dependence of the initial decomposition rates is given by the equation,

$$\ln R = -\frac{11100}{T} + 14.8168, \qquad \ldots(8)$$

where R is in grams per watt-hour and T is in °K. The corresponding activation energy is 22.1 kcal/mole.

Initial G values for the disappearance of ortho-terphenyl were calculated from the expression,

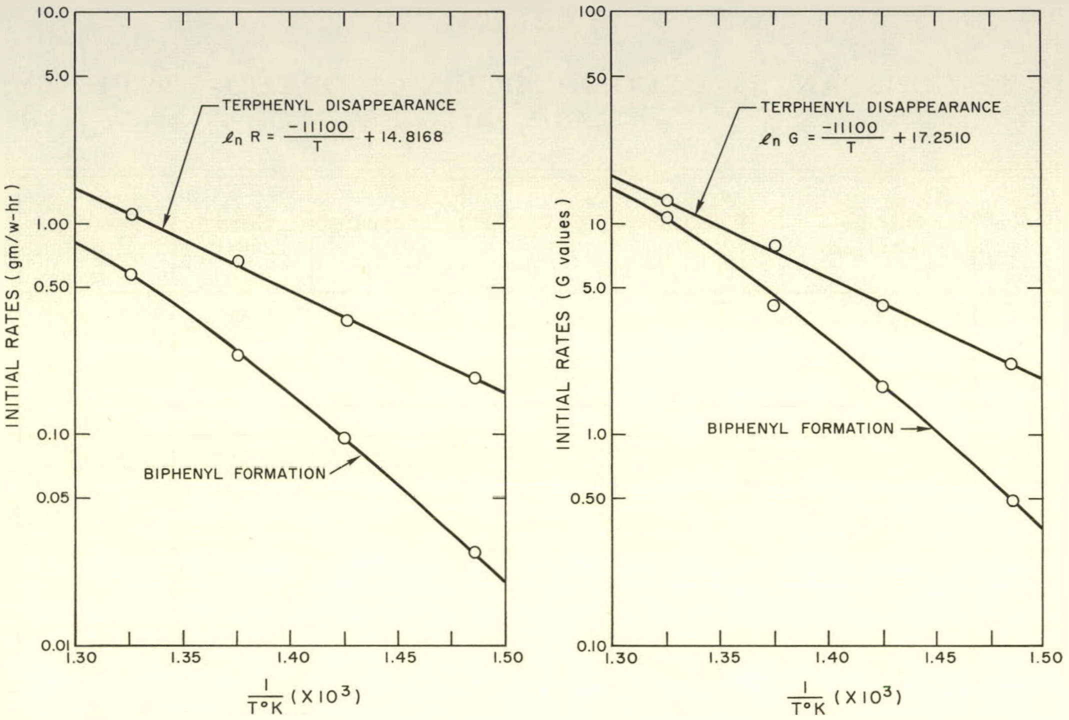
$$G_{(\phi_3)} = \frac{dy}{dD}\left(\frac{\text{gm}}{\text{w - hr}}\right)\frac{(6.02 \times 10^{23}\ \text{molecules/mole}) \times 100}{\left(\text{g-mol - wt}_{\phi_3}\right)\left(2.26 \times 10^{22}\ \text{ev/w - hr}\right)}, \qquad \ldots(9)$$

where dy/dD is the initial decomposition rate estimated graphically. These G values are shown in Table 6. The temperature dependence of the initial G values is shown in Figure 7.

TABLE 5

RATE CONSTANTS – DECOMPOSITION OF ORTHO-TERPHENYL (gm/w-hr)

Temperature (°F)	Dosage (w-hr/gm)	Weight Fraction 0 - ϕ_3 (1 - y)	First Order	Second Order	Third Order	Fourth Order	Fifth Order
752	0.419	0.923	0.190	0.199	0.207	0.216	0.225
	0.862	0.900	0.122	0.129	0.136	0.144	0.152
	1.296	0.862	0.114	0.123	0.133	0.144	0.156
	2.473	0.789	0.096	0.108	0.123	0.140	0.160
	3.342	0.749	0.086	0.100	0.117	0.137	0.163
	4.438	0.696	0.081	0.098	0.120	0.147	0.184
802	0.241	0.931	0.296	0.307	0.318	0.331	0.342
	0.541	0.866	0.265	0.286	0.308	0.333	0.360
	0.940	0.827	0.202	0.222	0.246	0.272	0.303
	1.071	0.823	0.182	0.201	0.223	0.247	0.275
	2.140	0.709	0.161	0.192	0.231	0.281	0.345
	4.766	0.568	0.119	0.160	0.220	0.312	0.452
850	0.431	0.815	0.473	0.526	0.588	0.655	0.737
	0.689	0.760	0.397	0.458	0.530	0.636	0.744
	1.310	0.673	0.302	0.371	0.461	0.580	0.738
898	0.445	0.752	0.639	0.741	0.862	1.01	1.20
	0.893	0.643	0.494	0.621	0.795	1.03	1.36
	1.252	0.595	0.414	0.543	0.729	1.00	1.39
	1.830	0.500	0.379	0.546	0.820	1.28	2.05



6-29-64 7500-1533

Figure 7. Radiolysis of Ortho-Terphenyl

C. BIPHENYL FORMATION

Since the data in Table 2 (plotted in Figure 8) for biphenyl formation cannot be represented by a simple analytical expression, the differential method as described above was used to determine the initial formation rates. Instantaneous formation rates for biphenyl ($d\phi_2/dD$) were determined graphically. The ln ($d\phi_2/dD$) was plotted against ln (1 - y) and the curve extrapolated to zero dosage in order to obtain the initial formation rates which are shown in Table 7.

The temperature dependence of biphenyl formation based on initial rates is shown in the Arrhenius plot in Figure 7.

Initial G values for the formation of biphenyl by all processes calculated from initial rates are tabulated in Table 7.

D. DISCUSSION OF RESULTS

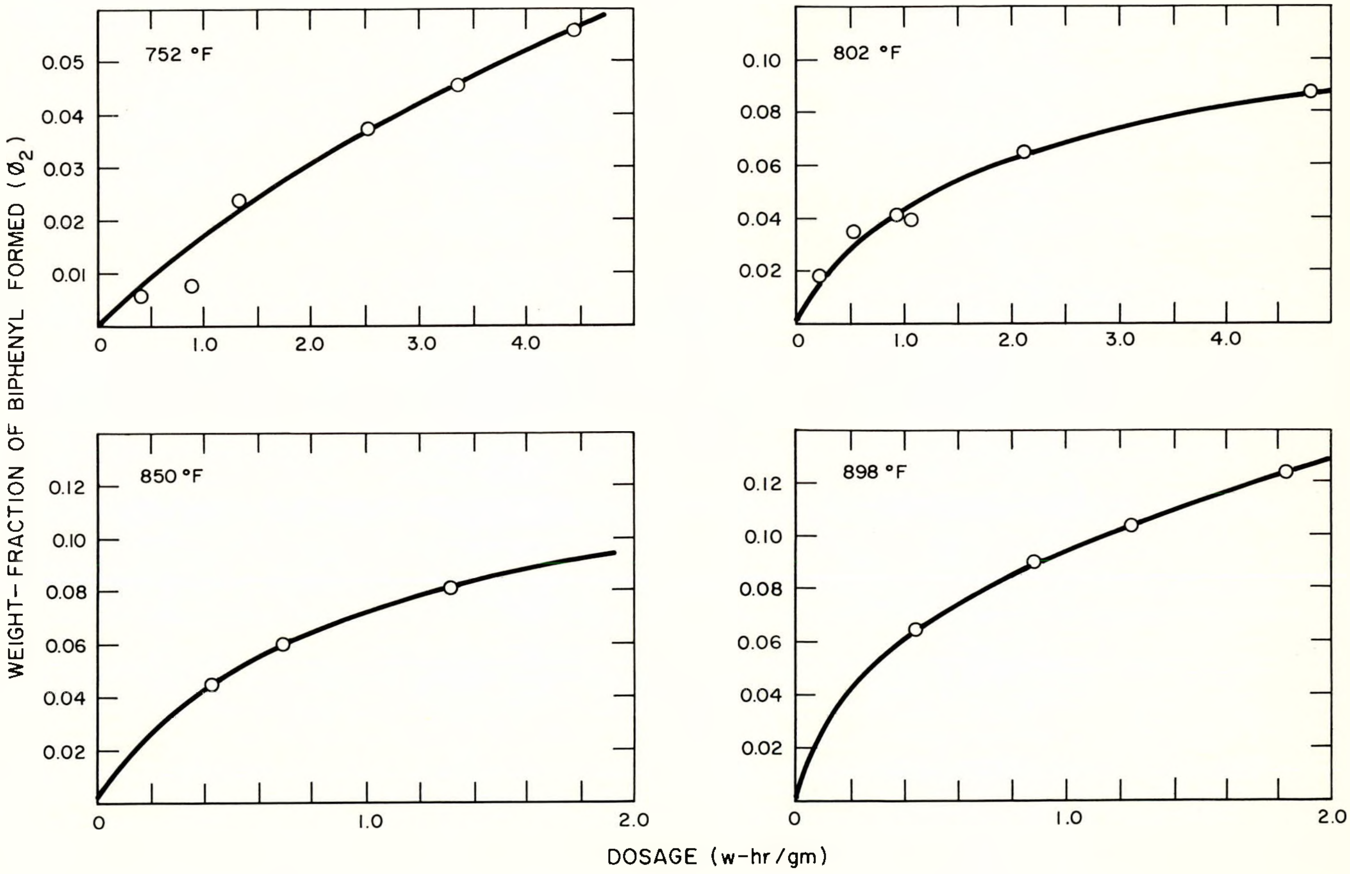
Several reports in the literature on the radiolysis of the polyphenyls contain a limited amount of information on the radiolytic decomposition of ortho-terphenyl. Although most of this information is not directly comparable to the current work, it is possible to make some limited comparisons.

TABLE 6

INITIAL DECOMPOSITION RATES FOR ORTHO-TERPHENYL

(1 Mev electrons)

Temperature (°F)	Initial $G_{(-o\ -\phi_3)}$
752	2.14
802	4.05
850	7.64
898	12.7



6-29-64

7500-1534

Figure 8. Radiolysis of Ortho-Terphenyl — Biphenyl Formation

TABLE 7

INITIAL BIPHENYL FORMATION RATES

Temperature (°F)	Initial Rate (gm/w-hr)	Initial $G_{(\phi_2)}$
752	0.0281	0.49
802	0.0973	1.68
850	0.235	4.06
898	0.577	10.0

Early data obtained at Atomics International[1] on the electron irradiation of ortho-terphenyl at 752°F indicated that $G_{(polymer)}$ values varied from about 0.065 at a dosage of 5 watt-hr/gm to 0.05 at 40 watt-hr/gm. Although $G_{(polymer)}$ values are not directly comparable to $G_{(-coolant)}$ values, it is quite obvious that the $G_{(polymer)}$ values above are in gross disagreement with the current work. The possibility of a systematic dosage error in the early Atomics International data, which resulted in low G values, has been discussed previously.[2] Later re-evaluation[12] of these data resulted in higher G values and brought agreement with the work of Bates et al.[2,10] It was concluded[12] that the initial electron $G_{(-coolant)}$ value for ortho-terphenyl at 600 to 750°F was approximately 0.2. It was also concluded that the "activation energy" for the electron radiolysis of ortho-terphenyl was about 0.95 kcal/mole; thus, the radiolytic decomposition rate for ortho-terphenyl should be almost independent of temperature.

The current investigation shows an initial $G_{(-coolant)}$ value of 2.14 for the electron radiolysis of ortho-terphenyl at 750°F. Also in contrast to the earlier work, this investigation has shown that the radiolytic decomposition of ortho-terphenyl is quite temperature dependent with an activation energy of about 22 kcal/mole. Based on the Arrhenius equation (Figure 7), the initial $G_{(-coolant)}$ value at 600°F is approximately 0.2, a value which is in agreement with the earlier data.[12]

In the gamma radiolysis of ortho-terphenyl[9] at 825°F, a $G_{(-\text{coolant})}$ value of approximately 4 (after correction for pyrolytic damage) was reported for a broad range of high-boiler concentrations. This value is in fair agreement with the current value of about 5.5 at 825°F, since any difference between the effects of gamma and electron irradiation should be negligible.

More recent publications of Atomic Energy of Canada, Ltd.,[17,18,19,20] report radiolytic decomposition rates for Santowax OM which may be compared crudely to those reported here. A rigorous comparison cannot be made because an isomeric mixture was used in the Canadian work and because the complete data are not available. In the Canadian work Santowax OM was irradiated at 707°F with 1 Mev electrons.[18] The dependence of $G_{(-\text{coolant})}$ on total dosage is demonstrated by the data shown in Table 8. It is obvious that $G_{(-\text{coolant})}$ values increase rapidly with decreasing dosage (decreasing damage) and that an initial G derived from the data would be greater than one. Indeed, the Arrhenius plot shown in Figure 7 shows that at 707°F the initial electron $G_{(-\phi_3)}$ should be about 1.2.

TABLE 8

RADIOLYSIS OF SANTOWAX OM,
CANADIAN DATA[18]

Dosage (watt-hr/gm)	$G_{(-\text{coolant})}$
4.34	0.328
4.34	0.316
6.50	0.247
6.50	0.221
8.72	0.184
8.72	0.218
8.72	0.248
13.1	0.156
17.4	0.156
26.1	0.100

This investigation shows clearly that the disappearance of ortho-terphenyl during radiolysis at high temperatures is strongly temperature dependent with an apparent activation energy of about 22 kcal/mole. This energy of activation is significantly higher than the 5 kcal/mole or less that is expected for free radical reactions. Therefore, it is suggested that one or more of the intermediate steps leading to the disappearance of ortho-terphenyl involves the thermal dissociation of radiolytically activated species not normally contributing to the decomposition of aromatic systems at lower temperatures. At the high ambient temperatures of these experiments, thermal spikes produced by the absorption of radiation could also enhance the thermal decomposition yields. A significant number of these dissociation reactions, which initiate additional radical chains involving the substrate, must be rate determining steps and could account partially for the high activation energy and for the very high G values observed.

In contrast to the simple mechanism proposed for biphenyl formation in the pyrolysis of ortho-terphenyl, any such mechanism for the formation of biphenyl in radiolysis would have to be complex. Data are not sufficient to permit realistic speculation on a possible mechanism. However, it is interesting to note that the processes contributing to the formation of biphenyl are a significant part of the secondary reactions resulting in the disappearance of ortho-terphenyl. The relative slopes of the Arrhenius curves for biphenyl formation and terphenyl disappearance indicate that biphenyl formation is more temperature dependent than terphenyl disappearance. This observation suggests that one of the ways in which biphenyl is formed involves the thermal decomposition of an intermediate.

Although no attempt will be made here to relate these electron irradiation studies to published work on neutron irradiation, it should be noted that it has been difficult to assign precise values to the "fast neutron effect".[12] It should also be noted that the reported temperature dependence for the decomposition of terphenyls in in-pile irradiations[9,10,11,12,21,22] is not nearly as high as that reported here for the electron irradiations. Furthermore, $G_{(-\phi_3)}$ values for electron radiolysis calculated from the Arrhenius equation derived here for temperatures near 600°F agree well with some of the G values for coolant disappearance reported for pile irradiations. A good example of this agreement is found in the in-pile loop studies performed at MIT[22] where a $G_{(-o\ -\phi_3)}$ value of 0.28 was established at 600°F. Perhaps the lack of data and the failure to assign enough importance to temperature effects are in part responsible for the uncertainty in assigning a precise value to the fast neutron effect. Another complicating factor in assessing fast neutron effects may arise from the possible existence of "micro or molecular" heating effects (thermal spikes) due to the deposition of kinetic energy from the neutrons. If such a condition exists, the temperature of individual molecules or groups of molecules may exceed bulk temperature. Thus, one of the consequences of fast neutron irradiation may be pyrolysis on a molecular scale or the thermal enhancement of radiolysis. Subsequent decomposition rates may thereby be increased. Since the bulk temperature may not be a true measure of temperature on a molecular basis, decomposition in a neutron field may appear independent of temperature, especially for the extreme case in which the temperature in the thermal spike is high enough to completely pyrolyze all of the substrate molecules in the track.

It is interesting to examine the practical consequences of extrapolating the Arrhenius curves shown in Figure 7 to higher temperatures. For example, at 1000 to 1100°F the G value for the disappearance of ortho-terphenyl would be approximately 35 to 85. Decomposition rates resulting at such temperatues and at higher dosage rates, up to several watts per gram, would be completely unacceptable for reactor coolant applications.

If the combined pyrolytic and radiolytic decomposition rates are compared to the pyrolytic rates only (by assuming that radiolysis and pyrolysis are additive) at corresponding temperatures, it is found that pyrolysis as such contributes only slightly to the total decomposition rate. Even at 900°F pyrolysis alone accounts for less than 6% of the combined radiolytic and pyrolytic rate, at a dosage rate of 0.8 w/gm.

IV. SUMMARY AND CONCLUSIONS

Due to the fact that this project was cancelled prematurely, many of the original goals were not achieved and in some cases the data are incomplete. However, sufficient data were obtained to establish the pyrolysis rate of ortho-terphenyl as a function of temperature up to 900°F and to establish the combined radiolytic and pyrolytic decomposition rates (initial and differential rates) as a function of temperature up to 900°F at a dose-rate of 0.8 w/gm using 1 Mev electrons.

The pyrolytic decomposition of ortho-terphenyl follows simple first order kinetics. Specific reaction rates were established at 786, 851, and 900°F and the activation energy for the thermal decomposition of ortho-terphenyl was found to be 71.7 ± 1.3 kcal/mole.

Biphenyl formation in pyrolysis probably follows first order kinetics and may be directly associated with the decomposition of ortho-terphenyl as the rate determining step; the activation energy for biphenyl formation is equal to that for ortho-terphenyl disappearance within experimental error.

This work establishes a temperature dependence for the radiolysis of ortho-terphenyl not clearly indicated in previous work. An activation energy of 22 kcal/mole was observed, which is significantly higher than that expected for a free radical process. Since free radical reactions normally proceed with activation energies of about 5 kcal/mole or less, it is suggested that one or more of the steps in the radiolytic decomposition involves thermal dissociations which are temperature dependent and partially rate determining.

REFERENCES

1. E. L. Colichman and R. Fish, "Pyrolytic and Radiolytic Decomposition Studies on Ortho-, Meta-, and Para-Terphenyls," NAA-SR-1287 (1955)
2. R. N. Wilkinson and T. H. Bates, "The Radiation and Thermal Stability of Some Potential Organic Moderator Coolants," AERE-M-412 (1959)
3. A. Houllier, "Pyrolyse du para-Terphenyle," French Atomic Energy Commission, DPC/PCA/61/50/AH/MD (1961)
4. D. R. deHalas, "Kinetics of Decomposition of Organic Reactor Coolants," HW-56769 (1958)
5. R. T. Keen, R. A. Baxter, L. J. Miller, R. C. Shepard, and M. A. Rotheram, "Methods for Analysis of Polyphenyl Reactor Coolants," NAA-SR-4356 (1959)
6. F. J. Sigurd Groennings, and J. J. Holst, Anal. Chem. 32, 904-909 (1960)
7. John G. Burr, J. M. Scarborough, J. D. Strong, R. I. Akawie and R. A. Meyer, Nucl Sci. & Eng. II, 218-226 (1961)
8. T. H. Bates, W. G. Burns, B. Morris, R. W. Wilkinson and J. F. Williams, "The Radiation and Thermal Stability of Some Potential Organic Moderator-Coolants, Part I. Electron Irradiation of para-Terphenyl and Santowax-R," AERE-C/R-2121 (1957)
9. R. H. J. Gercke and C. A. Trilling, "A Survey of the Decomposition Rates of Organic Reactor Coolants," NAA-SR-3835 (1959)
10. T. H. Bates et al, "The Radiation and Thermal Stability of Some Potential Organic Moderator Coolants, Part V, Pile Irradiations," AERE-R-3743 (1962)
11. W. G. Burns, C. R. V. Reed, R. W. Wilkinson, and J. A. Winter, "The Radiation and Thermal Stability of Some Potential Organic Moderator Coolants, Part VI, Effects of Temperature on Radiolysis," AERE-R-3989 (1962)
12. R. H. J. Gercke and J. F. Zack, "Coolant Decomposition Rates and Make-up Costs for Organic Reactors," NAA-SR-6920 (1962)
13. J. P. Manion and M. Burton, J. Phys. Chem. 56, 560 (1952)
14. M. Burton and W. N. Patrick, J. Chem. Phys. 22, 1150 (1954)
15. R. H. Schuler, J. Phys. Chem. 60, 381 (1956)
16. K. J. Laidler, Chemical Kinetics, (McGraw-Hill Book Co., New York, 1950)
17. W. D. Mackintosh, Progress Report, October 1 – December 31, 1961, Atomic Energy of Canada, Ltd., PR-CM-28
18. W. D. Mackintosh, Progress Report, January 1 – March 31, 1962, Atomic Energy of Canada, Ltd., PR-CM-29
19. W. D. Mackintosh, Progress Report, April – June 30, 1962, Atomic Energy of Canada, Ltd., PR-CM-30

20. W. D. Mackintosh, Progress Report, July 1 — September 30, 1962, Atomic Energy of Canada, Ltd., PR-CM-31

21. T. H. Bates et al, "The Radiation and Thermal Stability of Some Potential Organic Moderator Coolants, Part II, Pile Irradiations of para-Terphenyl and Santowax-R," AERE-C/R-2185 (1959)

22. D. T. Morgan and E. A. Mason, "The Irradiation of Santowax OMP in the MIT In-Pile Loop, Part I, Summary to October 5, 1961," MITNE-21 (1962)