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INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THE CHLORINATION OF MESITYLENE AND NAPHTHALENE
IN THE PRESENCE OF GAMMA RADIATION

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TABLE OF CONTENTS

ABSTRACT	1
INTRODUCTION	2
EXPERIMENTAL PROCEDURE	5
RESULTS	8
I. Details of the Mesitylene Reaction	8
A. The Substitution Reaction	9
B. The Addition Reaction	12
C. Temperature Effects	12
D. Product Analyses	17
II. Details of the Naphthalene Reaction	20
A. The Substitution Reaction	21
B. The Addition Reaction	21
C. Temperature Effects	25
D. Product Analyses	27
III. Radiation Yields	29
IV. Ratios of Addition Yields to Substitution Yields	30
DISCUSSION	32
SUMMARY	36
ACKNOWLEDGEMENT	38
BIBLIOGRAPHY	39

ABSTRACT.

The effect of gamma radiation on the rates of chlorination of mesitylene and naphthalene has been studied at a constant dose rate and at different temperatures. Rate data are presented for both the irradiated and non irradiated reactions and the results of product analyses are described.

The very rapid reaction of chlorine with mesitylene was found to be essentially unaffected by radiation under the conditions used and therefore, G values of zero were obtained both for the substitution and addition reactions. It was noted that the irradiated runs appeared to yield slightly different chlorinated products from the non irradiated runs.

The rate of chlorination of naphthalene was found to be greatly influenced by gamma radiation. Based on chlorine, maximum average G values of 566,000 for substitution and 680,000 for addition were obtained.

Several factors which affect the calculation of G values were presented and a new notation was used for the chlorination data. The current G values were calculated for consecutive time intervals throughout the reaction from the kinetic data.

INTRODUCTION

In the operation of nuclear reactors large amounts of radioactive fission products are obtained. In 1951 the University of Michigan initiated a broad program to discover uses for these fission products. Since one of the most predominant forms of radiation occurring in the fission products is gamma radiation, this laboratory has been concerned with the effect of this type of radiation on chemical reactions. The gamma radiation was obtained from cobalt-60 sources.

Of the many types of chemical reactions available, the polymerization and chlorination reactions were found to give appreciable yields of product in the presence of gamma radiation.

The influence of gamma radiation on the reaction of chlorine with aromatic compounds has been extensively studied in this laboratory. Benzene and toluene were among the first compounds to be chlorinated in the presence of gamma radiation. (1,2). Some data on the chlorination of xylene, ethyl benzene, mesitylene, and naphthalene have also been reported (3,4). However, the work on mesitylene and naphthalene was not comprehensive and this study presents new rate data, radiation yields, and product analyses for the chlorination of these two compounds.

It is known that mesitylene reacts readily with chlorine and that the chlorine content of the products varies proportionately with the length of time of the reaction.

Chlorine has been reported to react by substitution on the side chain, on the nucleus, or on both positions. No references to the addition reaction are generally made.

As many as twelve chlorine atoms have been substituted onto a mesitylene molecule by carrying out the reaction for approximately 340 hours at over 60°C (5). However, complete chlorination of the side chains often causes fission of the molecule with the formation of benzene hexachloride (6). Vapor phase chlorination (7) and photochemical liquid phase chlorination (6,8) favor direct substitution on the side chain. The latter methods employed ordinary light bulbs and diffuse light as the energy sources. The direct liquid phase chlorination of mesitylene with no control of the amount of heat or light has been shown to produce ring substituted products (9). Chlorinations using iron carrier with the exclusion of light have also yielded substitution on the ring (5). Often carbon tetrachloride was used as a solvent when relatively large amounts of the solid di- and trichloromesitylenes were desired.

Chlorine may react with naphthalene to form both addition (10) and substitution (11) products. However, the addition products lose hydrogen chloride upon heating to form substitution products. Thus, it is to be expected that the polychloro addition products will contain varying amounts of chloro substitution products depending on the conditions of preparation and purification.

Generally direct chlorination of solid naphthalene, molten naphthalene, or a solution of naphthalene in an appropriate solvent yields a mixture such as the 1-chloro, 2-chloro, 1, 4-dichloro, tetrachloro, and octachloro derivatives. Chlorination studies on naphthalene with iodine or iron filings as carriers and chlorobenzene or benzene as solvents have reported optimum yields of 1-chloronaphthalene (12,13,14). The 2-chloro isomer can be prepared directly from naphthalene by chlorination in the vapor phase (15).

Many dichloro and trichloro substitution products of naphthalene are known, but some of these derivatives cannot be prepared in good yield by direct chlorination. The chlorine atoms can occur in both rings.

The use of carbon tetrachloride as a solvent for naphthalene diminished the amount of naphthalene reacting but gave an increase in the yield of the higher chloro derivatives.

No significant data on the photochemical chlorination of naphthalene has been reported. An apparatus for the photochemical chlorination of naphthalene has been described but no data were presented (16). Ultraviolet radiation for this process was supplied by a mercury lamp.

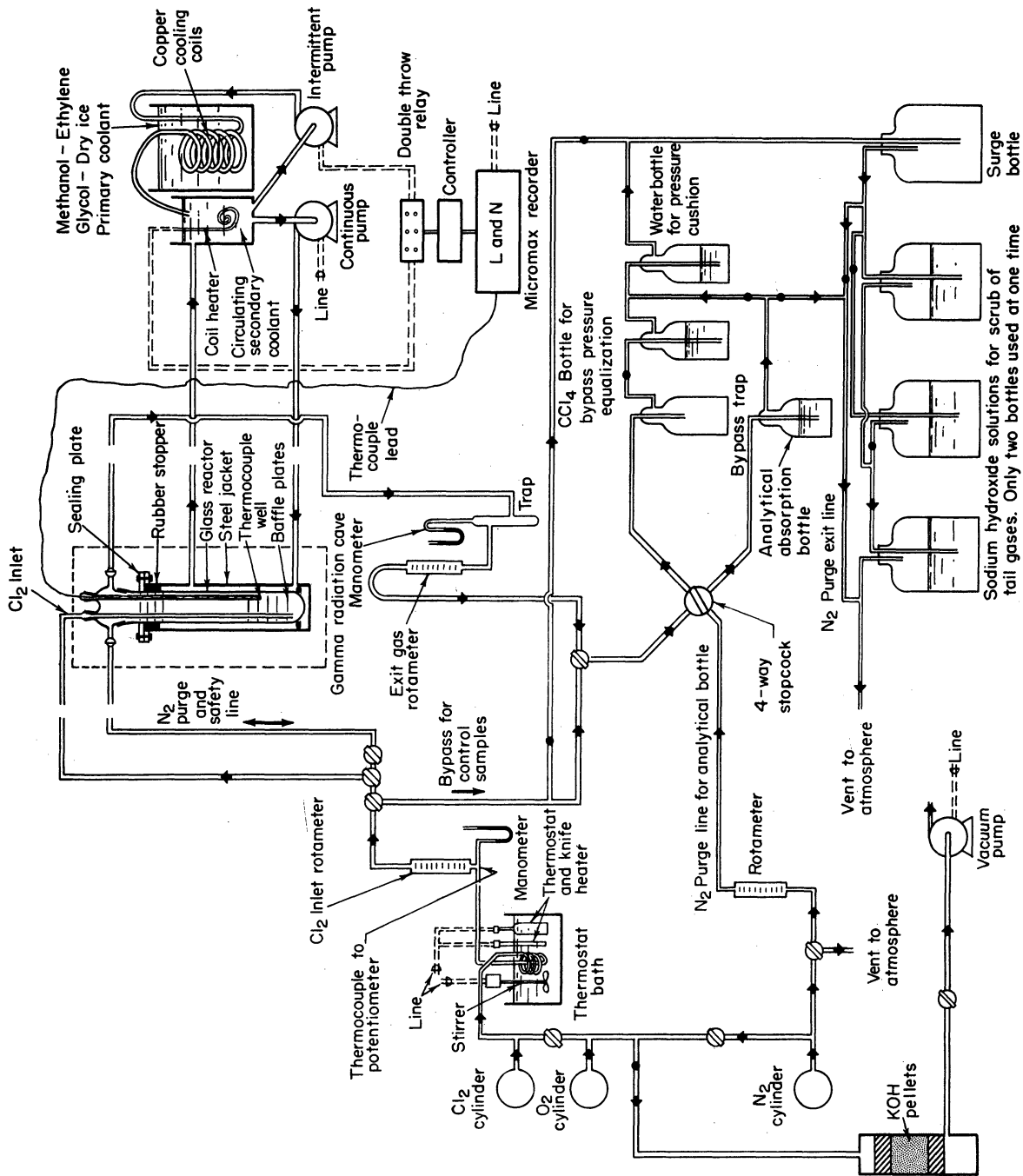
Polychloronaphthalenes containing five or more chlorine atoms are generally referred to as halowaxes and are usually prepared as a mixture of isomers. These compounds have aroused industrial interest as possible dielectric materials, ingredients in protective coatings, and constituents of plastics.

These applications have resulted in extensive studies on the halowaxes (17,18,19,20). A comprehensive study of the exhaustive chlorination of naphthalene has shown the catalytic effect of inorganic chloride carriers on the preparation of octachloronaphthalene (21).

EXPERIMENTAL PROCEDURE

A schematic diagram of the equipment used in this study is presented in Figure 1. This equipment is a modified form of that used by Harmer (2). The main features of the present technique are: (a) The chlorine inlet rate was maintained as constant as possible for a given series of runs; (b) The pressures in the system were carefully balanced such that a variation of less than 5 mm Hg occurred on switching from the bypass system to sample absorption; (c) Longer sample absorption times were used to decrease the errors from instantaneous pressure fluctuations; (d) Analytical procedures were held to a high precision; (e) A large capacity cooling system was used and the reactor cooling jacket was increased in volume. Prior to every run the entire system was successively evacuated and filled with pure nitrogen gas three times in order to remove any oxygen gas present. At the conclusion of each run, pure oxygen gas was introduced into the system to quench the reaction and to remove the dissolved chlorine gas in the reaction mixture.

The chlorine inlet gas flow rate was measured by a rotameter-type flow meter. This rotameter was calibrated with chlorine gas using both chemical absorption and titration and



• Haemostats for gas flow control

FIGURE 1. SCHEMATIC DIAGRAM OF THE EQUIPMENT USED IN THE CHLORINATION OF AROMATIC COMPOUNDS

measurement of gas volumes. The inlet gas temperature was measured with a thermocouple.

The reactor was placed in one standard position with respect to the gamma source for all runs in this study. An 1,800 curie cobalt-60 gamma source was used for all the experiments.

The exit gases from the reactor were absorbed through a fritted-glass dispersion tube in 0.2 N sodium arsenite in 3N potassium hydroxide solution. The absorption vessel was flushed with nitrogen gas before and after a sample was taken. The nitrogen gas was vented directly to the atmosphere to minimize pressure fluctuations in the reacting system. The sampling time was usually 3 or 4 minutes.

The reaction time was measured from the instant the gamma source was raised from the well to the midpoint of the exit gas absorption period.

The amount of free chlorine was determined indirectly by titration of an acidified aliquot of the arsenite solution with ceric sulfate. The amount of chloride ion was determined by the Volhard titration method using a second aliquot of the same arsenite solution.

Temperature control of the reacting system was maintained by a thermocouple recorder-controller. The thermocouple was calibrated with an ice bath prior to each run. Generally the variation in temperature was $\pm 1^\circ\text{C}$ throughout the whole run and in many cases the control was much closer to the set point.

The radiation dose rate was determined by ferrous

sulfate dosimetry (22). The conditions for dosimetry were exactly the same as those for an experimental run with the dosimetric solution replacing the aromatic in the reactor tube. The rates of chlorination of mesitylene and naphthalene were calculated by an overall chlorine material balance on the reacting system.

The reaction products were distilled in a simple vacuum distillation unit employing a Vigreux type column. Samples from each of the resultant distillate fractions were decomposed with sodium diphenyl reagent and subsequently titrated for total chloride by the Volhard method. In this way the total chlorine content was determined for each fraction.

RESULTS

Details of the Mesitylene Reaction

In all runs the reactor was charged with 60 ml (0.43 mole) of pure mesitylene. Because of the vigorous nature of the reaction it was not possible to saturate the mesitylene with chlorine. Runs conducted with a one minute sample absorption time were found to give large scatter of data points. An increase in the sample time to 3 or 4 minutes gave satisfactory results. The experimental conditions used are summarized in Table I and particular emphasis is placed on the constant chlorine inlet rate. An unusual temperature effect was observed during the reaction and is discussed later.

TABLE I Summary of experimental conditions used in the chlorination of mesitylene.

Run No.	Reaction Temp. M ^o C	Dose Rate Krep/hr.	Sample Time min.	Run Time min.	Chlorine Inlet Rate mM/min.
1	-5	none	4	53	22.6 - 22.9
2	-5	none	3	58	21.5 - 21.8
3	-5	none	3	53	22.0 - 22.3
4	-5	13.2	3	53	22.4 - 23.1
5	-5	13.2	3	29	22.0 - 22.1
6	20	none	4	65	22.3 - 22.5
7	20	13.2	3	53	22.3 - 22.4

The Substitution Reaction

Kinetic data for the substitution reaction at -5^oC are presented in Figures 2 and 3. Separate plots were made to illustrate the degree of duplication of the experimental method. Comparison of these two figures shows that there is no apparent effect of gamma radiation on the reaction rate.

Figure 4 presents the rates of substitution for irradiated and non irradiated runs at 20^oC. The curves were drawn separately and then superimposed to obtain the plot shown. Again the curves may be considered identical within the limits of experimental error.

All curves were graphically integrated to obtain the amount of chlorine reacted in ten minute intervals and these values appear in Table II. Examination of these data confirms the fact that radiation has no effect on the substitution reaction at the temperatures studied.

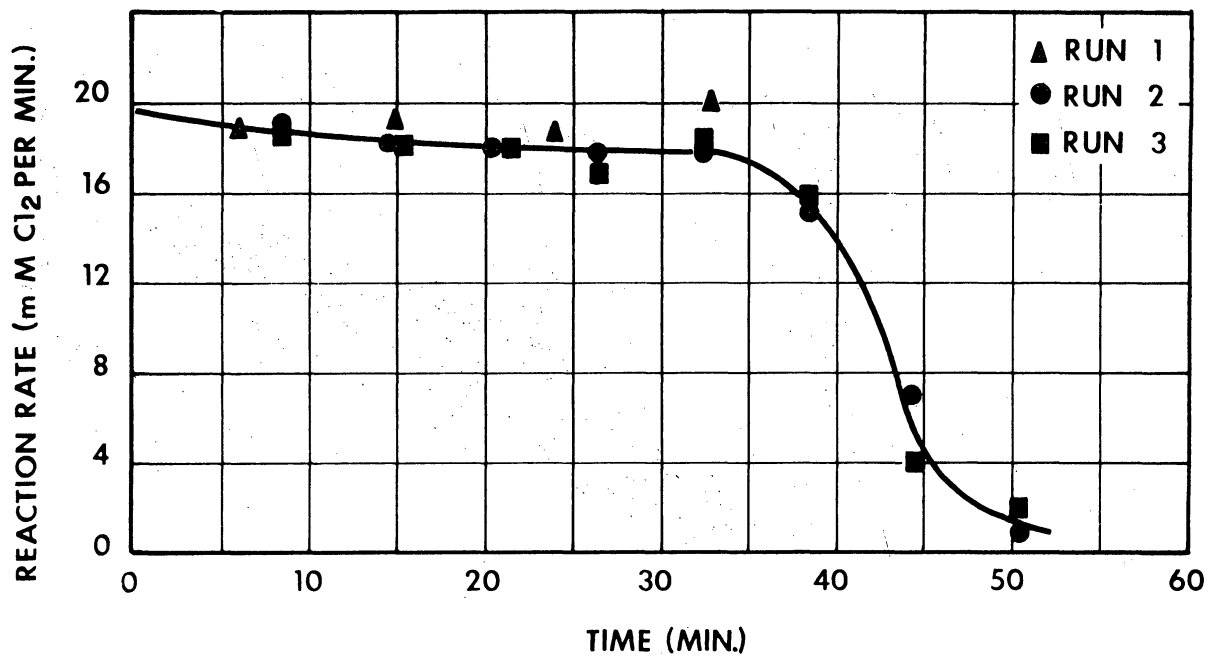


FIGURE 2. RATE OF CHLORINE SUBSTITUTION ON MESITYLENE AT -5 °C. (NON IRRADIATED)

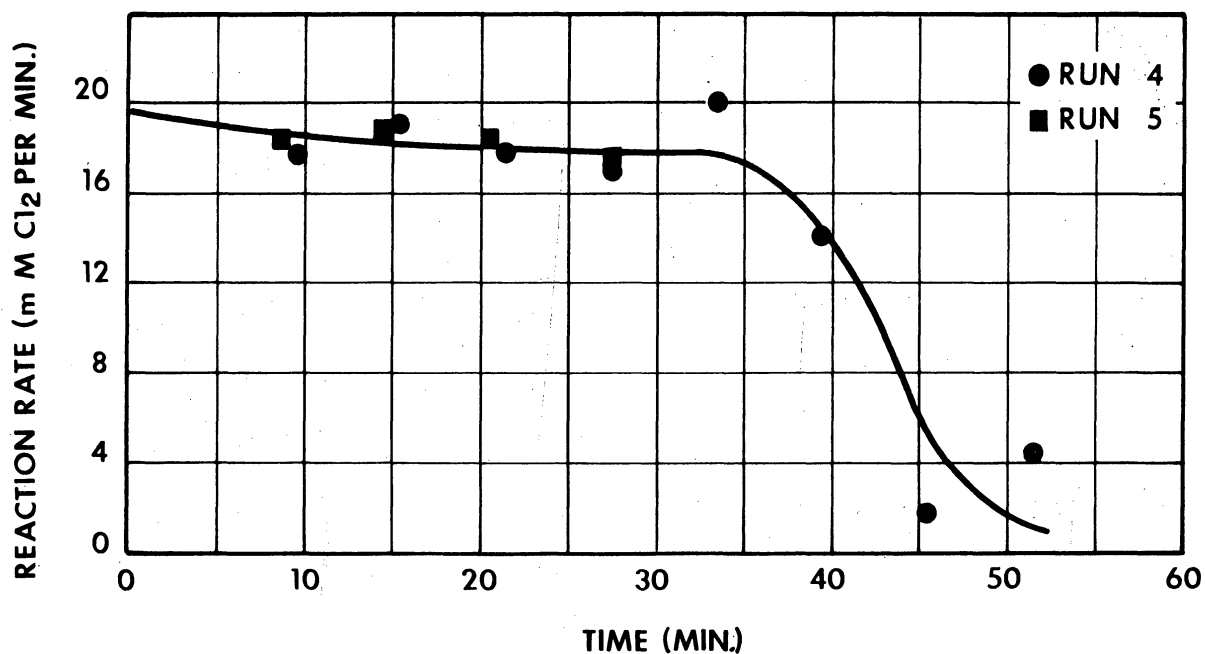


FIGURE 3. RATE OF CHLORINE SUBSTITUTION ON MESITYLENE AT -5 °C. (IRRADIATED)

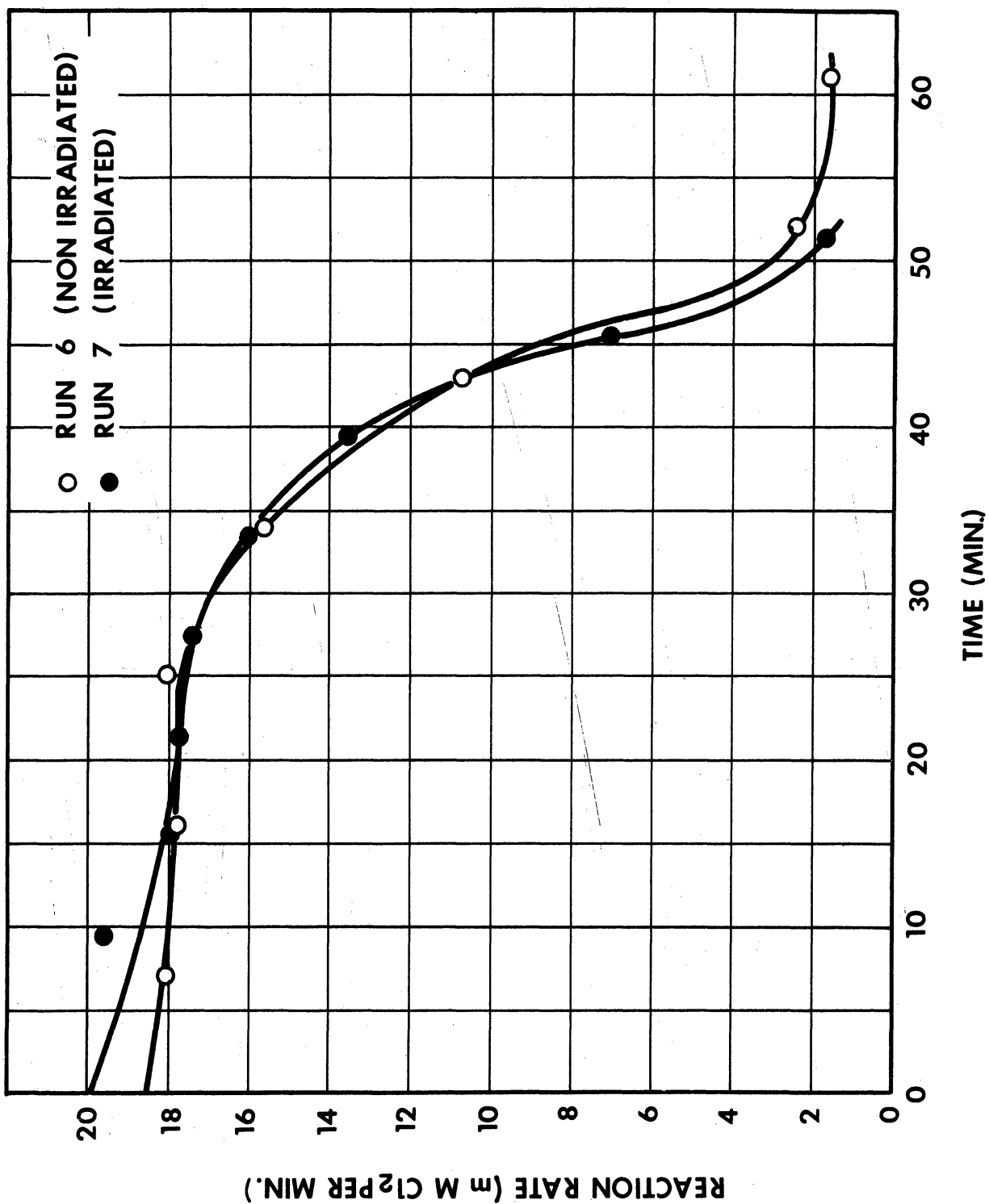


FIGURE 4. RATE OF CHLORINE SUBSTITUTION ON MESITYLENE AT 20°C

TABLE II Millimoles of chlorine reacted by substitution in successive time intervals during the chlorination of mesitylene.

Reaction Temp. °C	Dose Rate Krep/hr.	Millimoles of Chlorine, Time Intervals, minutes					Total
		0-10	10-20	20-30	30-40	40-50	
		-5	none	192	183	180	
-5	13.2	190	183	179	170	62	784
20	none	182	179	176	151	88	776
20	13.2	196	181	176	153	77	783

The Addition Reaction

Rate data for the addition reaction at -5°C and 20°C are shown in Figures 5, 6, and 7. All curves indicate an inductive effect for the addition reaction. In each curve the reaction rate is seen to increase to a maximum and then diminish. At both temperatures the curves of the irradiated runs show a slightly steeper initial slope than the curves of the corresponding non irradiated runs. However, the integration data of Table III show that the total amount of chlorine reacted is not influenced by the radiation at either temperature.

Temperature Effects

Examination of the mesitylene data shown that the substitution reaction is unaffected by a 25 degree change in temperature. This same temperature increase for the addition reaction resulted in a 22 percent increase in the total amount of chlorine reacted.

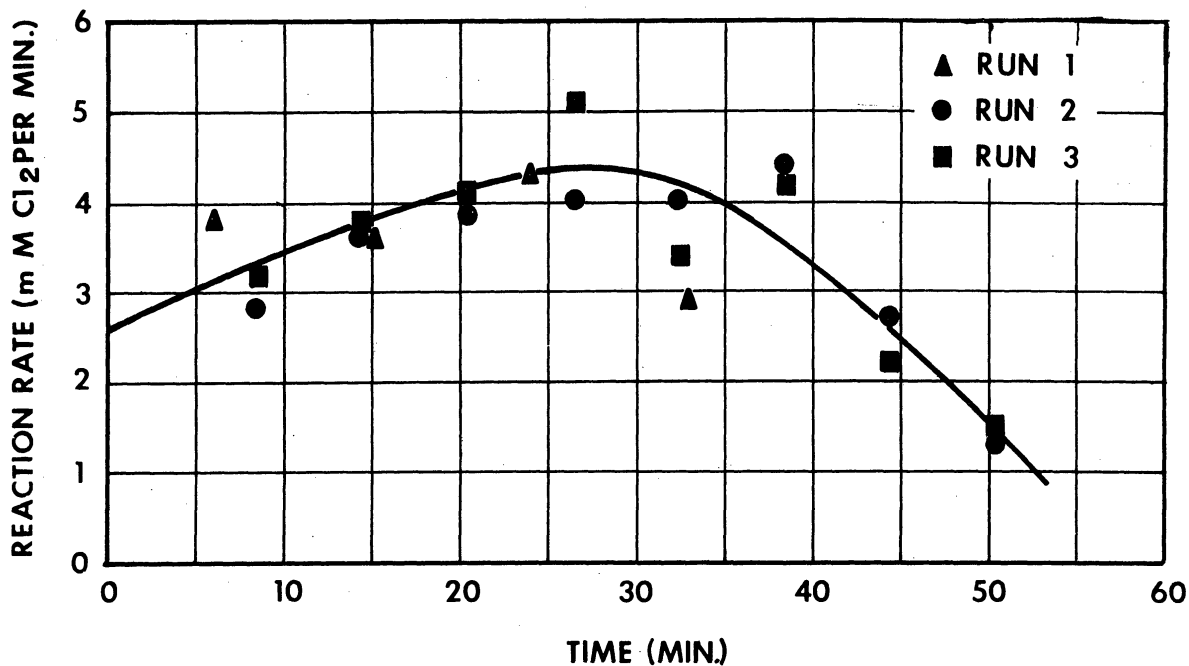


FIGURE 5. RATE OF CHLORINE ADDITION TO MESITYLENE AT -5 °C. (NON IRRADIATED)

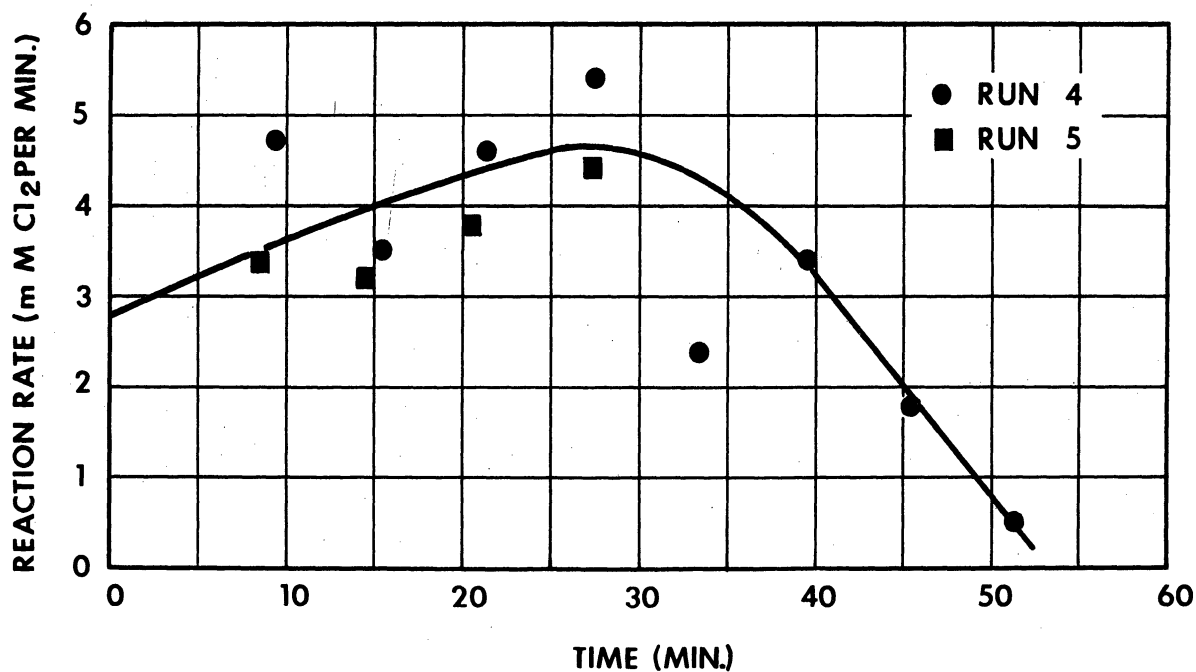


FIGURE 6. RATE OF CHLORINE ADDITION TO MESITYLENE AT -5 °C. (IRRADIATED)

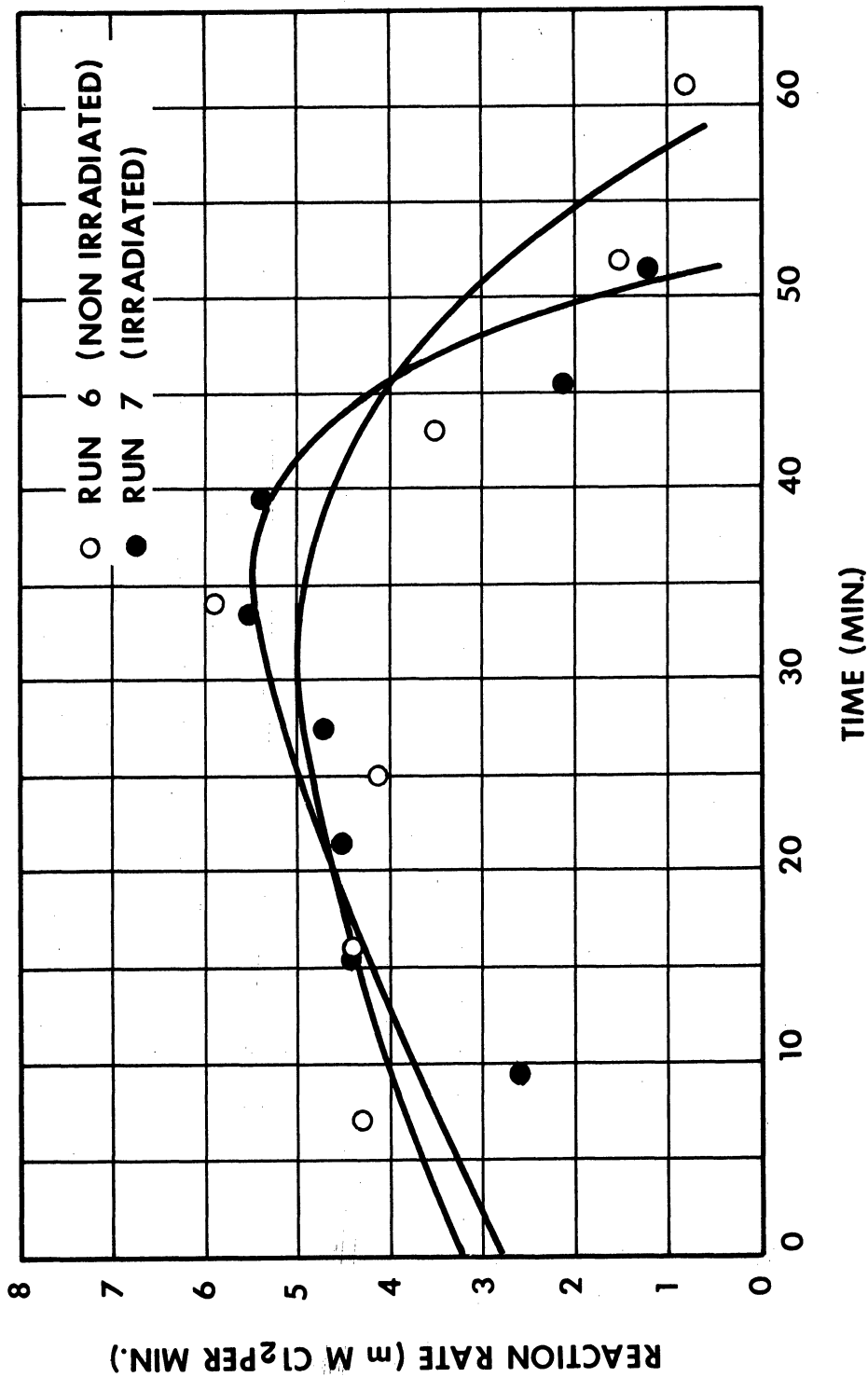


FIGURE 7. RATE OF CHLORINE ADDITION TO MESITYLENE AT 20°C.

TABLE III Millimoles of chlorine reacted by addition in successive time intervals during the chlorination of mesitylene.

Reaction Temp. °C	Dose Rate Krep/hr.	Millimoles of Chlorine					Total
		Time Intervals, minutes					
		0-10	10-20	20-30	30-40	40-50	
-5	none	29.5	37.5	42.0	38.8	24.5	172.3
-5	13.2	31.4	39.5	44.8	40.5	20.3	176.5
20	none	37.0	45.0	49.0	48.5	36.5	216.0
20	13.2	33.0	42.0	50.5	54.5	35.0	215.0

A peculiarity in temperature control was experienced in every mesitylene run. After a certain time the temperature of the reactor could no longer be controlled. This time was almost identical in runs at a given temperature. Table IV shows that after 34 minutes the temperature could not be prevented from rising in the runs conducted at -5°C . These times were somewhat longer for the runs at 20°C . The large amount of heat released from the reaction could not be removed quickly enough even with the maximum cooling capacity of the temperature control system. Figure 8 was composed to illustrate the position of this heat evolution with respect to the reactions taking place. It can be seen that the temperature rise corresponds to a decrease in the rate of the substitution reaction while the addition rate is still at the maximum value. An identical situation existed for all runs completed.

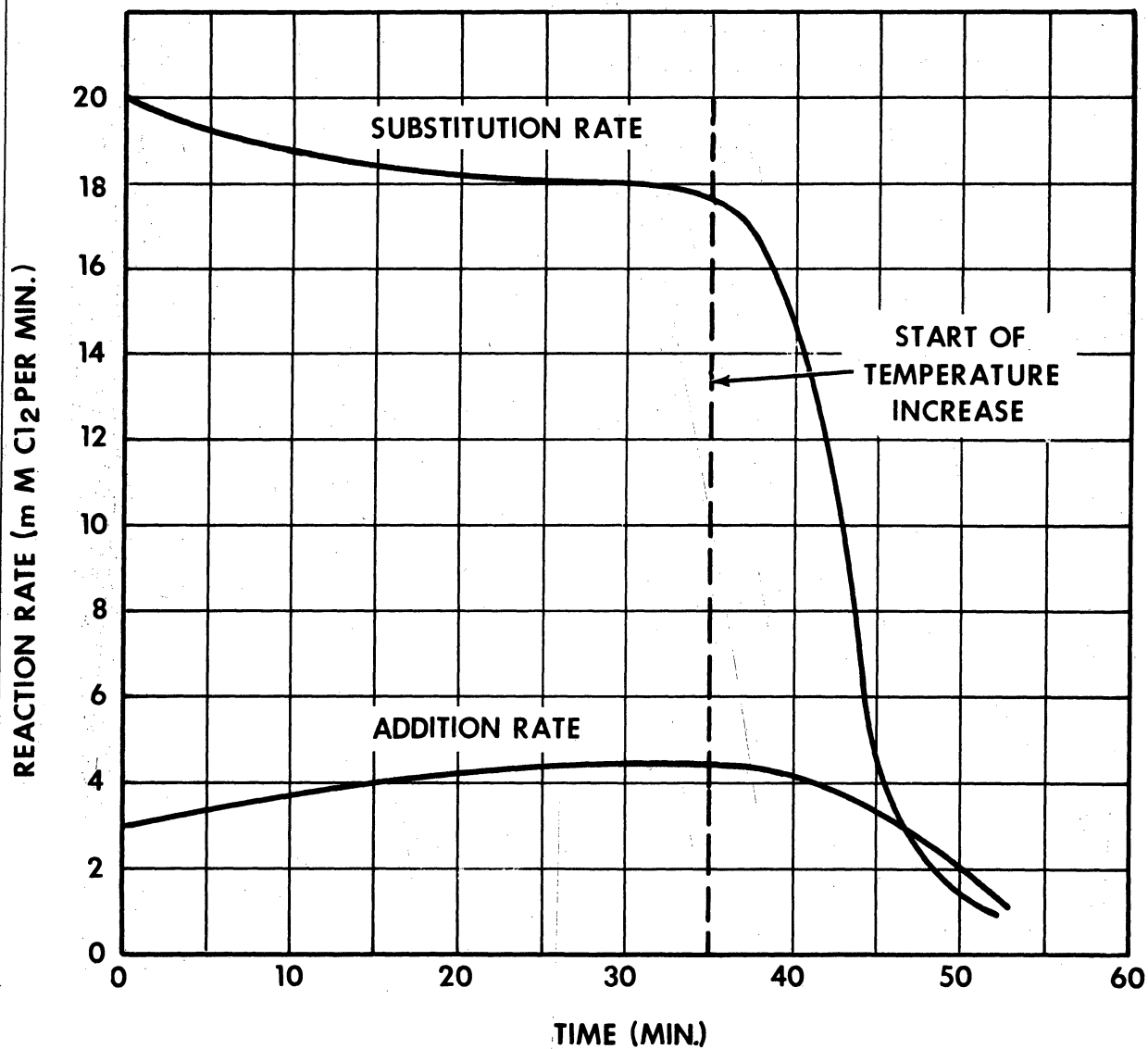


FIGURE 8. THE TIME AT WHICH THE REACTION TEMPERATURE STARTS TO RISE FOR THE NON IRRADIATED MESITYLENE RUNS AT -5°C . SIMILAR GRAPHS COULD BE DRAWN FOR IRRADIATED RUNS

TABLE IV Time after which the rising temperature in the reactor could not be controlled during the mesitylene runs.

Run Number	Reaction Temperature °C	Time of Temperature Rise min.
1	-5	34
2	-5	35
3	-5	35
4	-5	34
5	-5	*
6	20	37
7	20	37

* Run discontinued prior to temperature rise

The reproducibility of this temperature effect indicates that an explanation may lie in the nature of the two competing reactions. If it is assumed that the substitution reaction is endothermic in nature and the addition reaction is exothermic, then a temperature balance can exist between these reactions during the first part of the chlorination. However, a rise in the reaction temperature would be expected if the rate of substitution should decrease while the rate of addition remained nearly constant.

Product Analyses

All reaction mixtures from the chlorination of mesitylene were distilled under 0.3 - 1.6 mm. Hg pressure. Ether was used to aid the transfer of the reaction mixtures and was easily

removed under vacuum. The resultant distillate fractions were similar for all runs and no unreacted mesitylene was collected. The fractions consisted of colorless liquids and white solids or semi-solids. In a few cases a pale yellow color was observed. Total chloride analyses showed that the most abundant fractions were those analyzing for the mono-, di-, and tetrachloro derivatives. Some typical data are presented in Table V. It may be pointed out that the range in the theoretical percent chloride column of Table V is due to the possible formation of either substitution or addition products.

The majority of the still pot residues were dark orange in color and generally yielded higher total chloride content than any of the collected fractions. Also a strong odor of HCl was present in these residues. This would indicate that decomposition by dehydrohalogenation was occurring during the distillation. Thus it is reasonable to assume that the reaction mixtures initially contained higher chloro derivatives than those isolated.

With the exception of run 5, all runs at -5°C gave major distillate fractions which corresponded to the dichloro derivative. Colorless liquid fractions and white solid fractions corresponding to the mono- and tetrachloro derivatives respectively were next in abundance. No distinct fractions related to the trichloro derivative were obtained from the distillations. However, when a distillation was completed in the usual manner, some material usually solidified in the column and when isolated

TABLE V Typical data obtained from the distillation of chlorinated mesitylene reaction mixtures.

Type of Chloro Derivative	Theoretical Percent Chloride	Experimental Percent Chloride	Run Number	Fraction Number	Boiling Point Pressure mm. Hg.	Boiling Point Temp. °C	Fraction Volume ml.
Mono	23.0	20.4	6	I-B	0.6	29-31	0.7
		24.4	6	II-B	0.5	45-48	1.0
		23.1	7	I-B	1.5	48-49	1.9
		23.0	7	II-B	1.5	49-60	0.2
Di	37.2-37.6	37.7	6	III-B	0.6	65-67	3.5
		36.6	7	III-B	1.1	77-78	6.1
Tri	47.2-47.7	47.7	6	IV-B	Solid from column washings		-
		52.0	7	IV-B	Solid from column washings		-
Tetra	54.2-55.0	55.9	6	Pot Residue	-	-	-
		56.3	7	Pot Residue	-	-	-

gave an indication of being a trichloro derivative. Distillation of the reaction mixtures from the runs conducted at 20°C gave similar results.

It was noted that the irradiated runs gave larger yields of the higher chloro derivatives than the non irradiated runs. Also distillates from the irradiated runs were more clearly defined in boiling point range. It is possible that radiation may promote a selective type of chlorination but evidence for this is not conclusive.

Details of the Naphthalene Reaction

A solution of naphthalene in carbon tetrachloride was used in each of the experimental runs. This solution contained 10 grams of naphthalene and 90 grams of carbon tetrachloride. When the reactor was at the desired temperature chlorine gas was introduced at a rapid rate in order to saturate the carbon tetrachloride solution. After saturation was completed and the temperature was steady the gamma source was raised and chlorine gas was introduced at a predetermined rate. This was taken as zero time.

The reaction was studied at two temperatures, -5°C and 5°C. Irradiated runs at 20°C and 21°C were made to indicate the effect of temperature on the reaction rates. A summary of the experimental conditions is given in Table VI.

TABLE VI Summary of experimental conditions used in the chlorination of naphthalene.

Run Number	Reaction Temp. °C	Dose Rate Krep/hr	Sample Time min.	Run Time min.	Chlorine Inlet Rate mM/min.
8	-5	none	3	49	15.5-15.6
9	-5	13.2	3	49	15.0-15.1
10	5	none	3	49	15.3
11	5	none	3	49	15.0-15.2
12	5	13.2	3	49	15.2-15.5
13	20	13.2	3	49	14.9-15.0
14	21	13.2	3	36	15.0-15.4

The Substitution Reaction

Figures 9 and 10 show the effect of gamma radiation on the substitution reaction at -5°C and 5°C . At both temperatures an increase in reaction rate was demonstrated.

Table VII contains values from the graphical integration of the substitution curves in Figures 9 and 10. Also included in this table are values obtained at $20-21^{\circ}\text{C}$. At -5°C it can be seen that radiation effects a doubling of the total amount of chlorine reacted, and at 5°C , this amount is almost tripled.

The Addition Reaction

The effect of radiation on the rate of addition of chlorine to naphthalene is illustrated in Figures 11 and 12. An increase in reaction rate was observed for the irradiated runs at -5°C and 5°C . As in the case of mesitylene, the addition

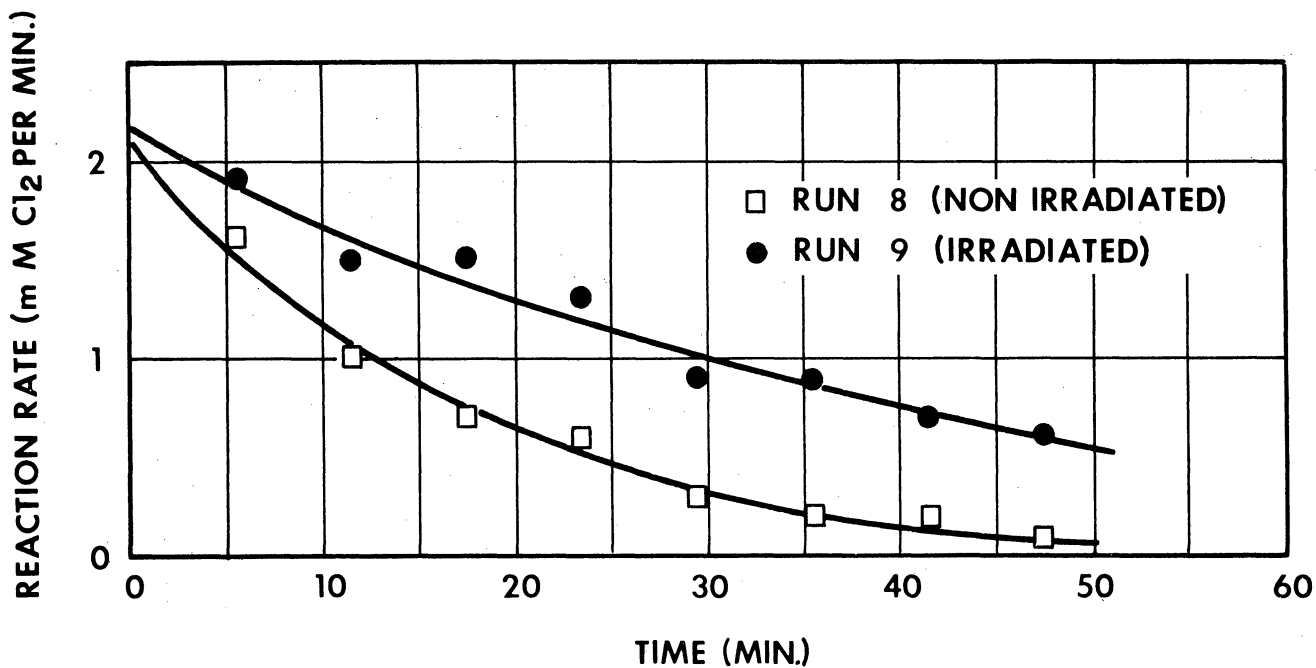


FIGURE 9. RATE OF CHLORINE SUBSTITUTION ON NAPHTHALENE AT -5 °C.

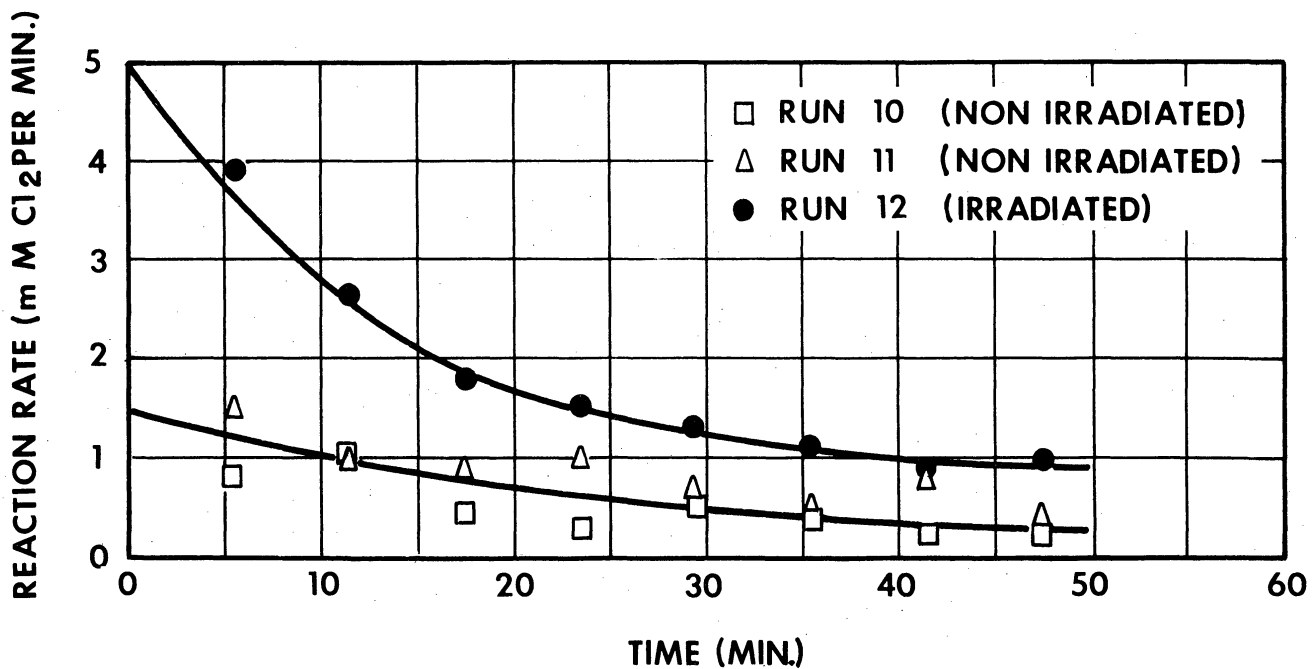


FIGURE 10. RATE OF CHLORINE SUBSTITUTION ON NAPHTHALENE AT 5 °C.

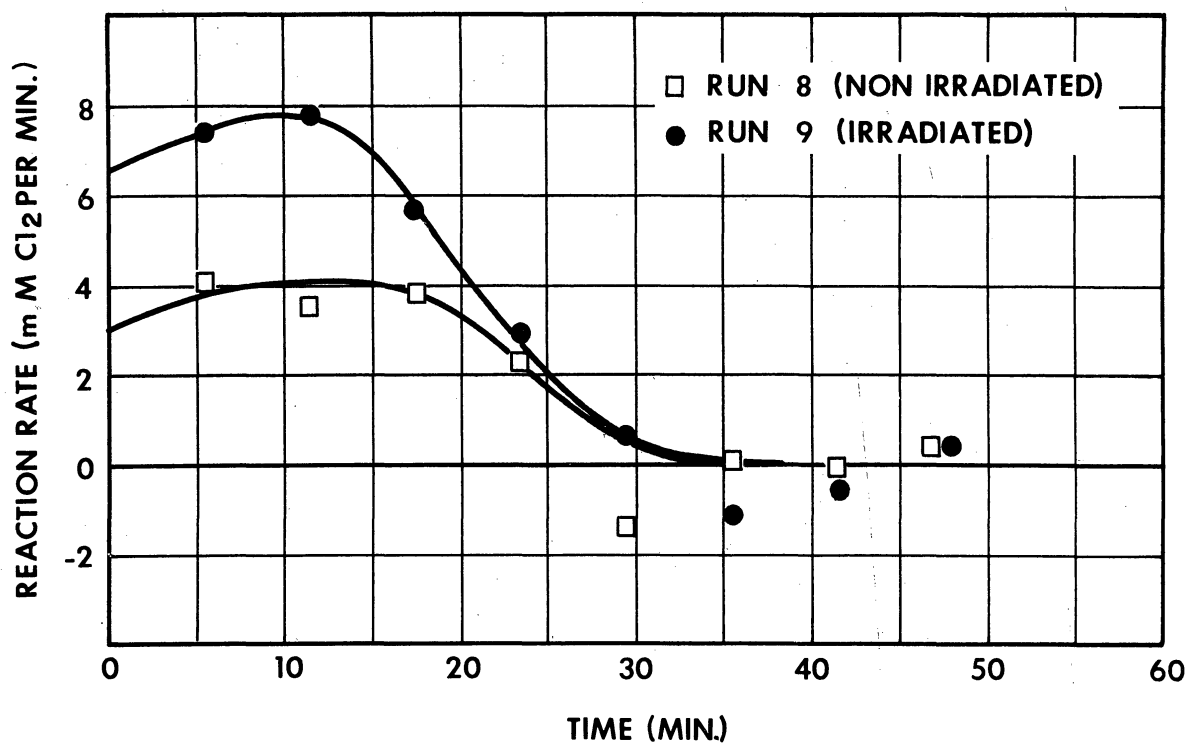


FIGURE 11. RATE OF CHLORINE ADDITION TO NAPHTHALENE AT -5 °C.

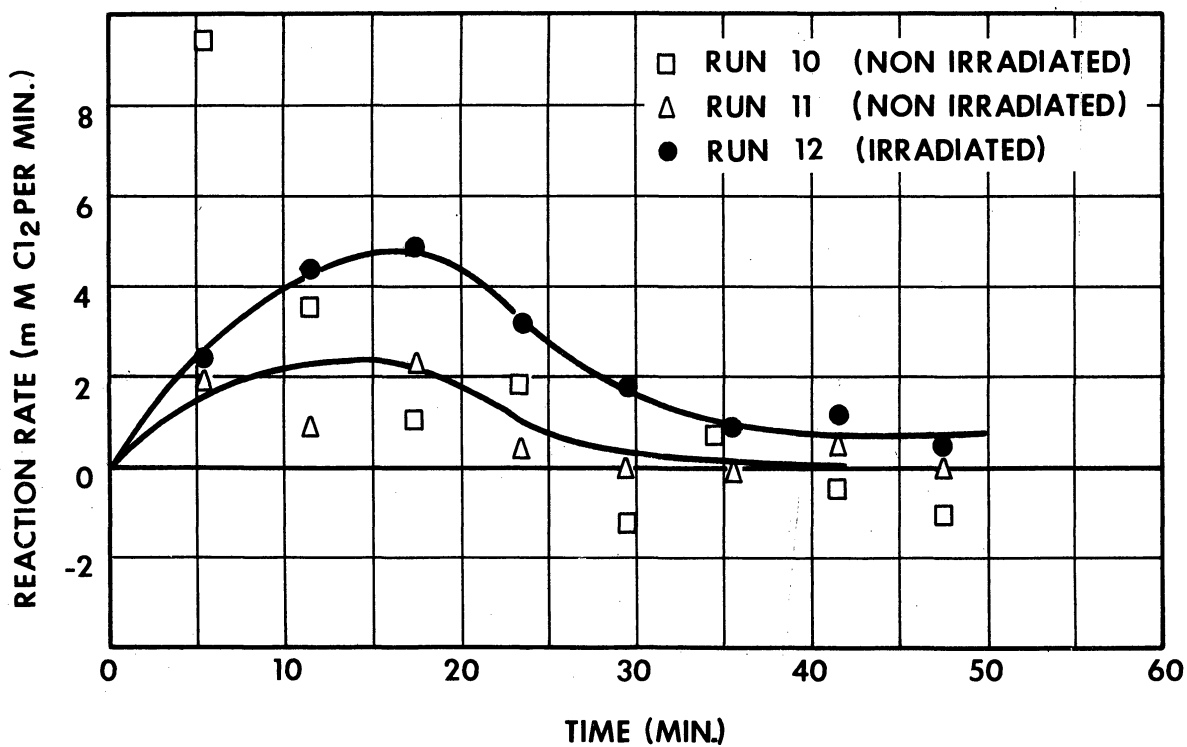


FIGURE 12. RATE OF CHLORINE ADDITION TO NAPHTHALENE AT 5 °C.

reaction again shows a period of induction during which the reaction rate increases to a maximum.

Values from the graphical integration of each curve shown in Figures 11 and 12 appear in Table VIII. Similar values obtained from irradiated experiments at 20-21°C are also given. For the overall reaction at -5°C and 5°C the amount of chlorine reacted is seen to increase about 1.5 and 2.5 times respectively when gamma radiation was employed.

TABLE VII Millimoles of chlorine reacted by substitution in successive time intervals during the chlorination of naphthalene.

Reaction Temp. °C	Dose Rate Krep/hr.	Millimoles of Chlorine Time Intervals, minutes					Total
		0-10	10-20	30-30	30-40	40-50	
-5	none	15.8	8.4	4.9	2.4	1.1	32.6
-5	13.2	19.5	14.9	11.5	8.8	6.4	61.2
5	none	12.3	8.5	6.0	4.3	3.1	34.2
5	13.2	38.1	21.5	14.3	11.2	9.5	94.6
20-21	13.2	16.8	11.3	8.2	6.1	5.5	47.9

TABLE VIII Millimoles of chlorine reacted by addition in successive time intervals during the chlorination of naphthalene.

Reaction Temp. °C	Dose Rate Krep/hr.	Millimoles of Chlorine Time Intervals, minutes					Total
		0-10	10-20	20-30	30-40	40-50	
-5	none	36.2	38.8	17.8	0.7	0.0	93.5
-5	13.2	73.0	66.0	22.9	1.8	0.0	163.7
5	none	12.0	21.3	8.7	1.5	0.0	43.5
5	13.2	22.0	45.0	31.3	10.4	7.4	116.1
20-21	13.2	6.9	15.4	11.0	3.5	2.0	38.8

Temperature Effects

In the chlorination of naphthalene, temperature was observed to have a large effect on the reaction rate. Over the temperature range studied, an increase in temperature resulted in a decrease in the rate of the addition reaction, while the substitution reaction rate was shown to reach a maximum value.

For the substitution reaction, the amount of chlorine reacted in the non irradiated runs was unaffected by a 10 degree change in temperature. On the contrary, for the irradiated runs the amount of chlorine reacted at -5°C increased by over 50 percent when the reaction temperature was raised to 5°C . Examination of Figure 13 reveals that the rate of substitution reaches a maximum at 5°C . It can be seen from Table VII that the total amounts of chlorine reacted by substitution at -5°C , 5°C , and 20.5°C are in the ratio of 1.3:2:1.

For the addition reaction, the total amounts of chlorine reacted in the non irradiated runs was shown to change by a factor of two when the temperature changed from -5°C to 5°C . Then for the irradiated runs these amounts decreased by almost 30 percent for the same temperature change. Figure 14 shows the rates of addition at three different temperatures. It can be seen that this rate decreases markedly with increasing reaction temperature. Reference to Table VIII will show that the total amounts of chlorine reacted at -5°C , 5°C , and 20.5°C are in the ratio of 4.2:3:1.

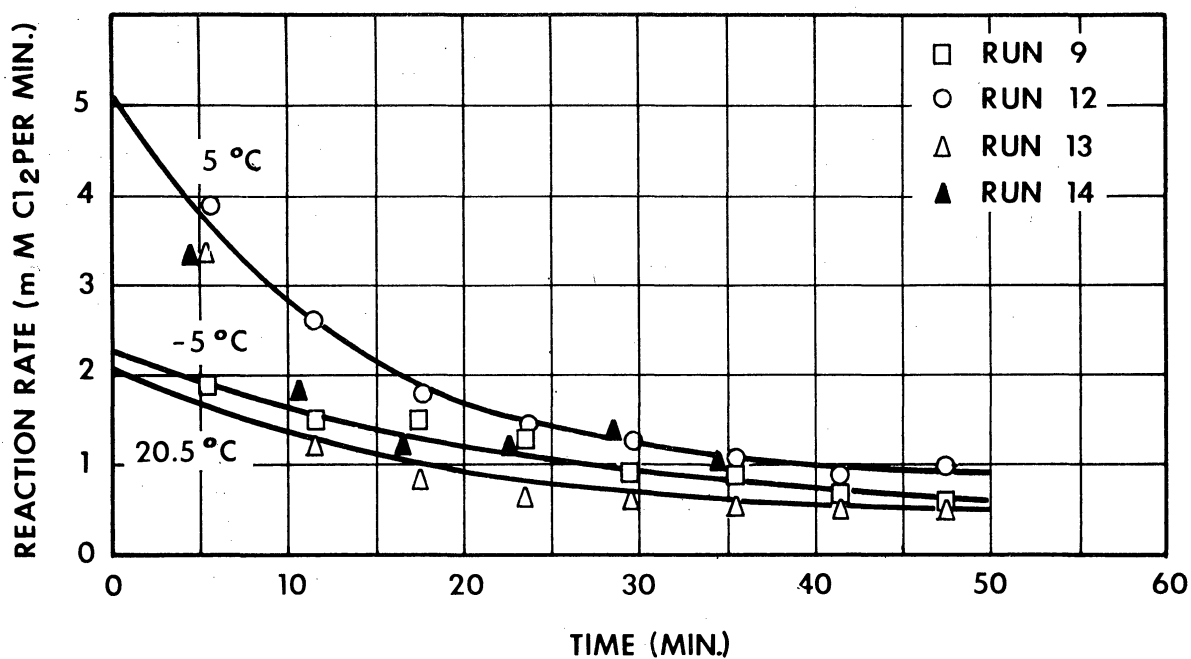


FIGURE 13. EFFECT OF TEMPERATURE ON THE RATE OF CHLORINE SUBSTITUTION ON NAPHTHALENE UNDER IRRADIATION.

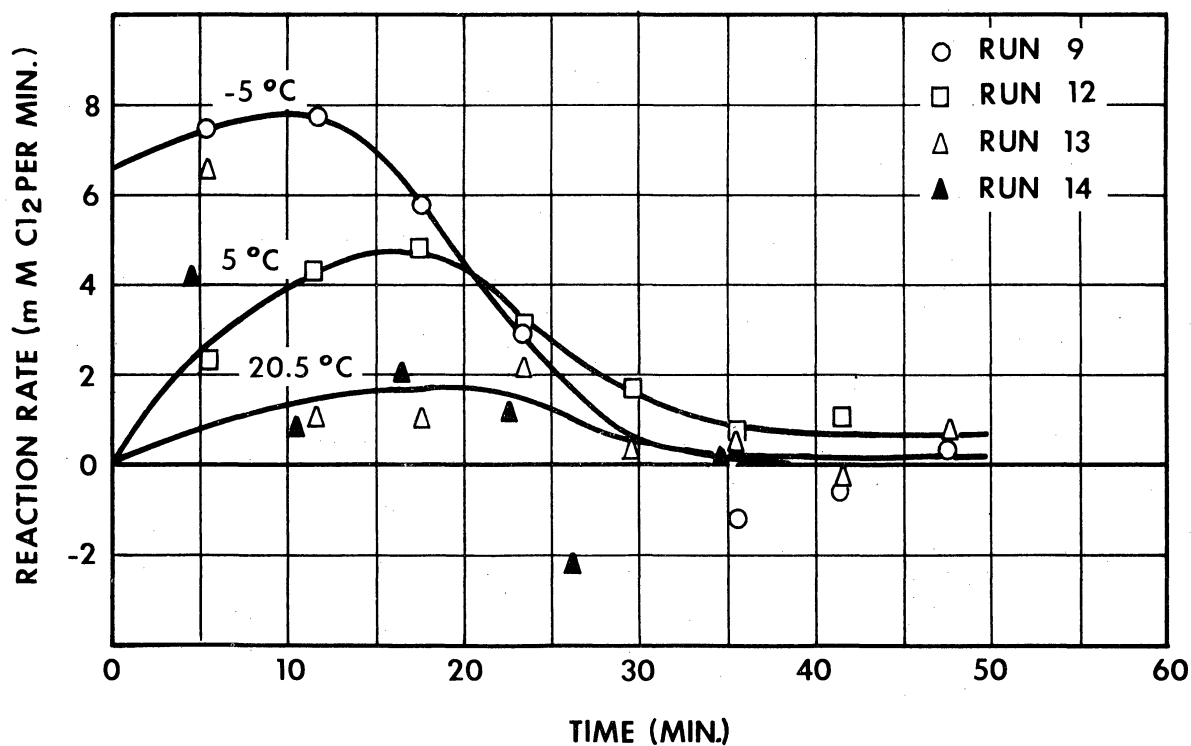


FIGURE 14. EFFECT OF TEMPERATURE ON THE RATE OF CHLORINE ADDITION TO NAPHTHALENE UNDER IRRADIATION.

The first points for the 20.5°C addition curve of Figure 14 are seen to be unusually high. A similar tendency is noted for the corresponding substitution curve of Figure 13. It is believed that, at a low reaction rate, the reacting system takes a long time to reach stable equilibrium conditions. Hence more scatter may be expected during the first portion of the reaction and this is reflected in data for both the substitution and addition reactions.

Product Analyses

The reaction mixtures from the chlorination of naphthalene were distilled under vacuum. The carbon tetrachloride solvent was removed at about 3-6 mm Hg. pressure. Thereafter the distillations were continued at a pressure of about 1 mm. Hg. An assortment of distillate fractions resulted from each run and no unreacted naphthalene was isolated. Some typical data are presented in Table IX. The range in the theoretical percent chloride in this table is due to the possible formation of either substitution or addition products.

Although the results indicated nothing higher than a tetrachloro derivative, it is probable that higher polychloro derivatives were formed since the odor of HCl was detected in some of the residues obtained from the distillation. Again decomposition by dehydrohalogenation was indicated.

TABLE IX Typical data obtained from the distillation of chlorinated mesitylene reaction mixtures.

Type of Chloro Derivative	Theoretical Percent Chloride	Experimental Percent Chloride	Run Number	Fraction Number	Boiling Point Pressure mm. Hg.	Temp. °C	Fraction Volume ml.
Di	35.6-36.0	37.1	8	I	1.1	102-107	-
		39.1	9	I	1.2	117-122	1.0
		39.1	10	II	0.4	91-93	1.5
		36.6	12	II	0.3	90-96	4.2
Tri	45.6-46.0	46.3	8	IV	0.5	110-111	1.9
		46.4	9	II	0.8	117-126	1.6
		46.7	10	III	0.3	94-108	0.8
		45.5	12	IV	0.5	95-126	1.4
Tetra	52.6-53.4	53.2	8	VI	0.4	123-134	2.8
		52.8	9	V	0.7	128-134	1.1
		52.5	10	VIII	0.4	123-133	3.1
		50.8	12	V	0.6	123-131	2.8

The range in the theoretical percent chloride in this table is due to the possible formation of either substitution or addition products.

The runs at -5°C and 5°C gave distillate fractions of similar appearance. No monochloro derivatives were obtained and no fractions were obtained above 144°C . At both temperatures fractions analyzing for the di-, tri-, and tetrachloro derivatives were obtained. The irradiated run at -5°C showed a higher yield of the tri- and tetrachloro derivatives than the non irradiated run. However, at 5°C , the irradiated run showed a predominance of the trichloro derivative.

Fractions analyzing for the di- and trichloro derivatives were colored. When freshly distilled, white solids or colorless liquids were obtained. Upon standing a short while a change to pink solids and mauve liquids was observed. Recrystallization of the solid fractions established that the pink solid was in reality a mixture of a white solid and a pink to mauve liquid. Total chloride analyses indicated that these were the di- and trichloro derivatives respectively.

The runs at 20°C and 21°C gave distillate fractions quite different in appearance from those at the other temperatures. Again similar chloro derivatives were obtained. Run 13 gave evidence of a monochloro derivative but this was the only case. Light green and orange distillate fractions were obtained but these color effects were not investigated further.

Radiation Yields

Examination of Tables II and III shows that there was no radiation yield for the chlorination of mesitylene. Within the limits of experimental error G values of zero were obtained

for both the substitution and addition reactions. This does not mean that the radiation was without effect because the irradiated runs appeared to yield slightly different chlorinated products from the non irradiated runs. It would appear that under our experimental conditions, the reaction was so rapid in the absence of radiation that we could not detect a quantitative difference in chlorine uptake when radiation was employed.

The radiation yields for the chlorination of naphthalene are expressed in terms of G values based on chlorine and these appear in Table X. The calculation of these G values for specific time intervals makes possible several interesting observations. The G values for substitution are almost constant throughout the run at -5°C but show a comparatively high value during the early stages of the reaction at 5°C . For addition, the G values are highest during the first 30 minutes of the reaction. The addition reaction at -5°C is virtually unaffected by radiation after 40 minutes. The overall or average radiation yield for addition is almost identical at both temperatures.

Ratios of Addition Yields to Substitution Yields

It has been of interest to examine the ratios of the addition yields to the substitution yields for the reactions studied. These ratios have been calculated for mesitylene and naphthalene and are shown in Table XI. Examination of this table shows that under our experimental conditions the ratio of the total amount of chlorine reacted by addition to that reacted

TABLE X G values based on chlorine for the chlorination of naphthalene.

Reaction Temp. °C	Type of Reaction	G Values Based on Chlorine					Overall for 50 min.
		Time Intervals, minutes					
		0-10	10-20	20-30	30-40	40-50	
-5	Substitution	173,000	304,000	309,000	299,000	253,000	268,000
5	Substitution	1,210,000	608,000	388,000	323,000	300,000	566,000
-5	Addition	1,720,000	1,270,000	239,000	51,500	0	658,000
5	Addition	468,000	1,110,000	1,060,000	416,000	346,000	680,000

by substitution was not affected by radiation. For mesitylene, this ratio was little affected by a 25 degree rise in reaction temperature. However, for naphthalene, this ratio was decreased by a factor of two with a 10 degree rise in the reaction temperature.

TABLE XI Ratios of addition yields to substitution yields at various temperatures obtained from the chlorination of mesitylene and naphthalene for a 50 minute reaction time.

Aromatic Compound Chlorinated	Reaction Temp. °C	Ratios of Addition Yields to Substitution Yields	
		Non Irradiated	Irradiated
Mesitylene	-5	0.22	0.23
Mesitylene	20	0.28	0.28
Naphthalene	-5	2.9	2.7
Naphthalene	5	1.3	1.2

DISCUSSION

It is customary to report the yields of radiation reactions in terms of "G" values (molecules reacted per 100 electron volts of radiation absorbed). The G values calculated for the chlorination of benzene and toluene were based on the actual number of moles of chloro products obtained per kilogram of reactants (1,2). These G values were calculated for reactions in which a product of known chemical composition was formed and in which little or no product formation was observed without radiation.

In this report a different approach to the presentation of radiation yields has been adopted. Although it is important not to overemphasize the G value, we felt it necessary to point out the importance of the time factor in its calculation. Also, in any given reaction, the G value calculation may be based either on the formation of a product of known chemical composition or on the disappearance of one of the reactants. The current calculations were based on the amount of chlorine reactant used during the various experimental runs.

For the chlorination of mesitylene and naphthalene, it was not possible to determine all of the actual products that were formed. Several different products were formed, probably simultaneously and at different rates. Hence, the G values presented were based on the net amount of chlorine gas which reacted under the influence of gamma radiation. This net amount of chlorine was obtained by subtracting the rates of the non irradiated runs from the rates of the irradiated runs when said runs were conducted under otherwise identical conditions. These G values based on chlorine are larger than those calculated for the formation of a definite chloro compound. For example, the G values presented for naphthalene would be diminished by the mole ratio of chlorine to naphthalene involved in the reaction. If the ultimate yield on complete chlorination resulted in 2 moles of chlorine adding and 4 moles of chlorine substituting per mole of naphthalene, then the corresponding G values based on chlorine

would be reduced by a factor of 2 and 4 respectively. Furthermore, it is thought that the calculation of G values for small time intervals would present more useful information and would enable one to properly evaluate other G values reported in the literature.

Inspection of the naphthalene data showed that it is desirable to be explicit in the quotation of a G value. It is possible that the calculation of an average G value can be misleading. For this reason it is suggested that a G value should have certain descriptive information attached to it. The following notation is designed for the current calculations but could have general application:

$$G_{10} \text{ (addition, } -5^{\circ}\text{C)} = 1,720,000$$

$$G_{10-20} \text{ (addition, } -5^{\circ}\text{C)} = 1,270,000$$

$$\text{and } G_{50} \text{ (addition, } -5^{\circ}\text{C)} = 658,000$$

The subscript refers to the time over which the calculation was made or the specific time interval. The brackets contain the type of reaction and the temperature.

These data illustrate that the overall G value for 50 minutes (G_{50}) does not show that the maximum radiation yield was obtained during the first 10 minutes of the reaction. Also, an overall or average G value may vary depending on the particular time used in the calculations. In order to make valid comparisons among G values found in the literature, it would appear that several factors pertaining to the actual calculation should be specified in conjunction with the reported G value.

Earlier G values for the chlorination of mesitylene and naphthalene, which are not in agreement with the present data, have been reported from this laboratory (3,4). This discrepancy arises from several factors. First, correction for the rate of the non irradiated reaction was not included in the earlier calculations. Second, the earlier calculations were not made for comparable time intervals. Last, the naphthalene values were based on 100 grams of reactant rather than 1000 grams. For these reasons the present data are believed to be superior.

In previous work, reaction products were not isolated and generalizations on the nature of the reactions which had occurred were based on the benzene and toluene reactions (3,4). Hence, it was reported that addition of six chlorine atoms and alkyl substitution appeared to be the primary reactions with mesitylene and that the ratio of the addition reaction yield to the substitution reaction yield appeared to be increased by radiation and decreased by increasing temperature. In the present work, hexachloro addition compounds were not isolated in the case of mesitylene and no conclusions could be drawn regarding their possible formation. Also our study shows that the above ratio is not affected by radiation under the experimental conditions employed but in the case of naphthalene, this ratio does appear to be decreased by increasing temperature.

SUMMARY

1. An experimental method has been established which gives reproducible results and detects small changes in reaction rates during the continuous chlorination of an aromatic compound.
2. The rates of chlorination of mesitylene and naphthalene have been measured under irradiated and non irradiated conditions.
3. For the chlorination of mesitylene and naphthalene, kinetic data show that reaction occurs both by substitution and by addition.
4. Gamma radiation was found to show no effect on the rate of chlorination of mesitylene under the experimental conditions used, but it appears to show a small effect on the type of chlorinated product formed.
5. The rate of chlorination of naphthalene was found to be greatly affected by gamma radiation.
6. The effect of temperature on the rate of chlorine addition to naphthalene was determined. In particular, the addition reaction was favored by low temperature and therefore, it appears that the reaction rate is a function of the chlorine concentration in the reaction mixture.
7. All present experiments show that the ratio of the addition yields to the substitution yields was not affected by radiation.

8. Radiation yields expressed as G values based on chlorine have been calculated for the reactions studied. In the case of mesitylene, G values of zero were obtained both for the substitution and addition reactions. For naphthalene, maximum average G values of 566,000 for substitution and 680,000 for addition were obtained.

9. Several factors affecting the calculation of the G value have been discussed. Results from this study show that quotation of an average G value may be misleading because it is dependent on the time over which the measurements are made.

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