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THE CHLORINATION OF M-XYLENE AND METHYL
NAPHTHALENES IN THE PRESENCE OF GAMMA RADIATION

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INTRODUCTION

INTRODUCTION

In 1951 the University of Michigan initiated a broad program to discover uses for the radioactive fission products which are obtained in large amounts from the operation of nuclear reactors. Several groups in this laboratory have directed their efforts toward finding chemical reactions that are promoted by radiation. One of the principal forms of radiation given off by the fission products is gamma radiation. As no fission products were readily available, cobalt-60 sources of gamma radiation were employed in all studies.

The selection of chemical reactions for thorough study was governed by either or both of the following general objectives: (a) To study reactions of commercial or possible commercial importance which are promoted by radiation; (b) To study reactions of a general kind which might aid in explaining the mechanism of radiation effects. The chlorination of aromatic hydrocarbons was one of the chemical reactions which was investigated extensively. This paper presents the final experimental work on the chlorination studies conducted in this laboratory.

The effect of gamma radiation on the reaction of chlorine with benzene and toluene was reported from this laboratory by Harmer (1,2). Recently, further work was reported on the chlorination of mesitylene, naphthalene, and ethyl benzene (3,4). The current data on m-xylene, 1-methyl naphthalene, and 2-methyl naphthalene are presented to extend and complete the series of aromatic compounds which have been chlorinated in the presence

of gamma radiation. In this study, kinetic data, product analyses, and radiation yields for the chlorination of these three aromatic compounds are presented at one temperature and one radiation dose rate. The radiation yields are expressed in terms of "G" values (molecules reacted per 100 electron volts of radiation energy absorbed). The product analyses are not exhaustive and are designed to indicate generally what type of reaction products were obtained.

Investigations of the reaction of chlorine with xylene have generally involved the use of a pure isomer as a starting material. If a mixture of isomers was used, identification of the reaction products was somewhat more difficult. Direct chlorination of xylene may result in (a) substitution on the side chain, (b) substitution on the ring, or (c) addition to the ring. These reactions were found to occur singly or in combination.

Chlorination of all three pure isomers of xylene and commercial xylene mixtures have been reported in the literature. Photochemical methods, both in the liquid and vapor phases, have resulted in chlorination of the side chains (5,6,7,8). Nuclear substitution reactions have been affected by the use of catalysts such as ferric chloride and iron (9,10,11,12,13,14). The reaction of chlorine with xylene by addition has been reported under special conditions (6,15). The addition of chlorine to m-xylene occurred during low-temperature chlorination. Upon warming the addition product, HCl was given off and substituted m-xylenes were formed with two chlorine atoms in the aromatic

nucleus (15). The reaction of chlorine with a xylene mixture has been reported to proceed both by substitution and by addition in the presence of gamma radiation (16,17).

No significant data on the photochemical chlorination of naphthalene or its methyl derivatives have been reported. A kinetic study of the chlorination of naphthalene in the presence of gamma radiation has been reported earlier from this laboratory (3). In this earlier study literature references for previous work on the chlorination of naphthalene have been presented.

EXPERIMENTAL PROCEDURE

A complete description of the procedure and equipment used in the chlorination studies has been presented in a previous report (3). A short summary of the general method is given below.

The rates of chlorination of m-xylene, 1-methyl naphthalene, and 2-methyl naphthalene were calculated by an overall chlorine material balance on the reacting system. The inlet chlorine gas flow rate was measured with a calibrated flow meter. Samples of the exit gases from the reactor were taken periodically throughout the experiment. The amount of unreacted chlorine gas and the amount of chloride ion in each exit gas sample were determined by chemical methods.

The radiation used in all the experiments was supplied by an 1,800 curie cobalt-60 gamma source. The radiation dose rate was determined by ferrous sulfate dosimetry (18).

The reaction mixtures from each run were distilled in

a simple vacuum distillation unit. Chemical methods were used to determine the total chlorine content of each distillate fraction.

RESULTS AND DISCUSSION

The results obtained from the chlorination of m-xylene, 1-methyl naphthalene, and 2-methyl naphthalene are presented in three separate sections. A summary of the experimental conditions used in the three reactions is shown in Table I. In all the runs, the chlorine inlet rate showed a slight variation among the samples. However, during the taking of any given sample, the chlorine inlet rate was constant.

TABLE I. Summary of experimental conditions used in the chlorination of m-xylene, 1-methyl naphthalene, and 2-methyl naphthalene at -5°C .

Run No.	Compound Reacted	Dose Rate Krep/hr.	Sample Time min.	Run Time min.	Chlorine Inlet Rate mM/min.
1	m-xylene	none	3	69	21.6-21.7
2	m-xylene	60.3	3	68	21.4-21.6
3	1-methyl naphthalene	none	3	59	14.8-14.9
4	1-methyl naphthalene	60.3	3	59	15.0-15.1
5	2-methyl naphthalene	none	3	60	15.0-15.1
6	2-methyl naphthalene	60.3	3	60	15.0-15.1

I. Reaction of m-xylene

A. Details of the reaction

For each run the reactor was charged with 60 ml (0.49 mole)

of dried and distilled m-xylene. The m-xylene used was Eastman Kodak white label grade number 275.

The reactor temperature was brought to -5°C before the run was started. When chlorine was first admitted to the reactor a 3-4 degree rise in temperature occurred. Some 4-5 minutes later the temperature suddenly rose 27 degrees more. At this point a vigorous flow of exit gases from the reactor was noted and the odor of HCl was detected. The temperature of the reactor was brought back to the control setting in 6-7 minutes by the recorder-controller.

A sharp temperature drop of 6-8 degrees occurred about 29-31 minutes after the run was started. It will be seen later that this temperature drop corresponded with a sharp decrease in the rate of substitution. Thus, this temperature effect suggested that the substitution reaction could be exothermic in nature.

B. Kinetic data

The kinetic data obtained for the reaction of chlorine with m-xylene by substitution are shown in Figure 1. Smooth reaction rate curves were obtained for both the irradiated and non irradiated runs. A very high reaction rate was observed for the substitution reaction. Within the limits of experimental error, no effect of radiation on the substitution reaction was demonstrated.

Figure 2 shows the rate of chlorine addition to m-xylene. These data illustrated that radiation had essentially no effect

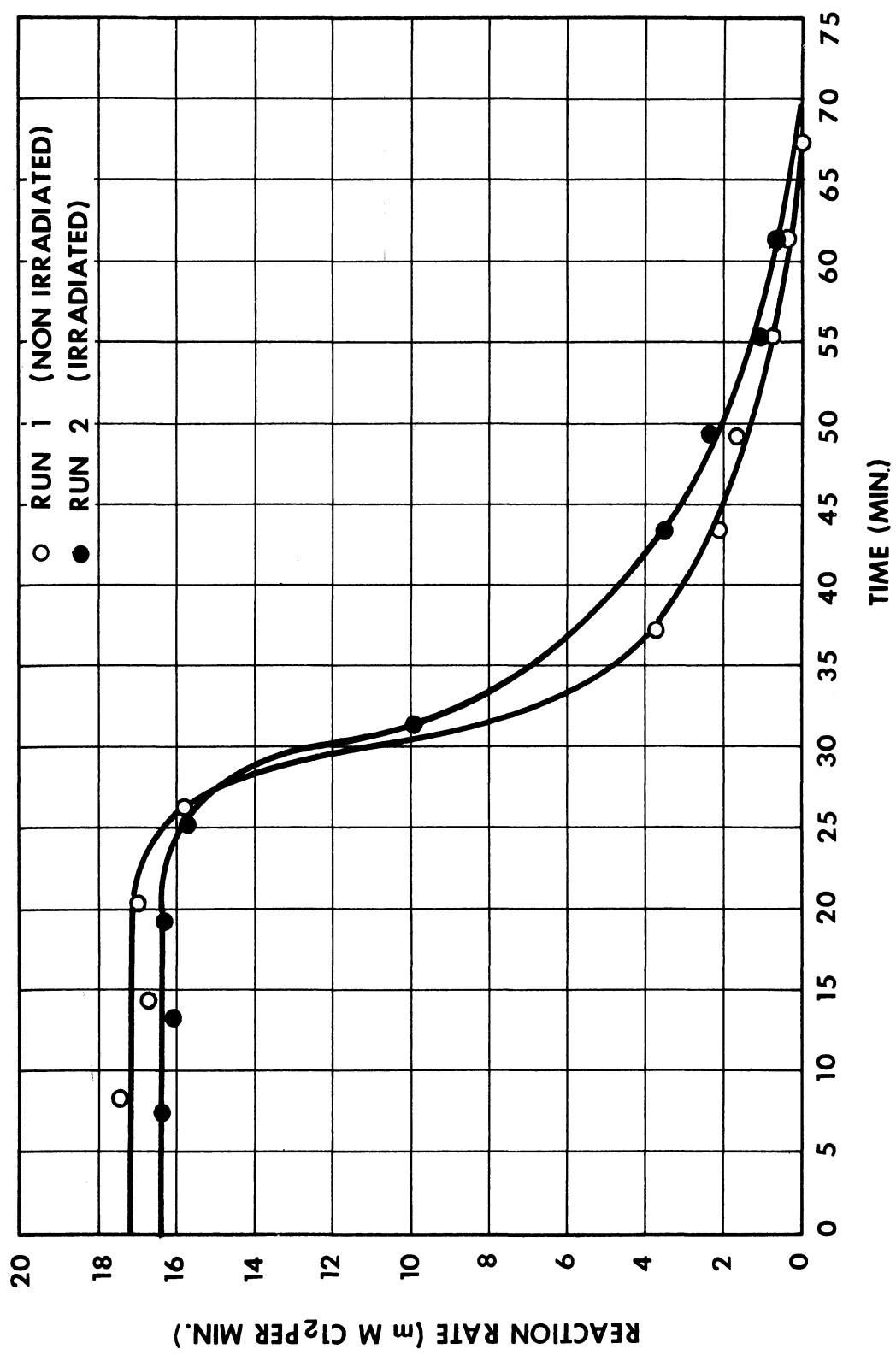


FIGURE 1. RATE OF CHLORINE SUBSTITUTION ON META-XYLENE AT -5° C.

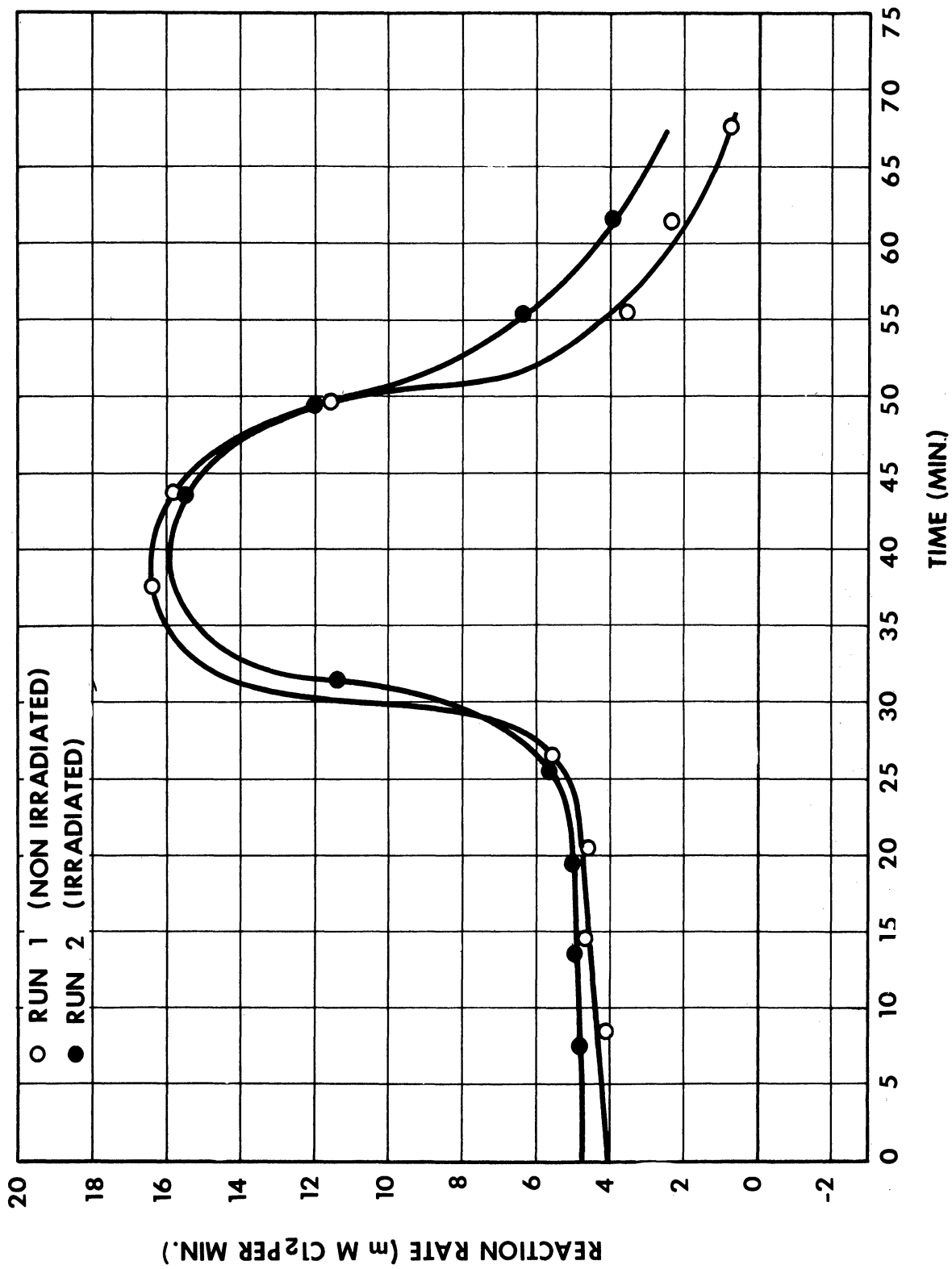


FIGURE 2. RATE OF CHLORINE ADDITION TO META-XYLENE AT -5° C.

on the addition reaction. Both reaction rate curves showed a large and abrupt rise in the middle of the reaction. This rise in the addition reaction rate coincided with a marked decrease in the rate of substitution. Again, as in earlier studies (3,4), there was an indication that the substitution reaction occurred preferentially.

Each curve of Figures 1 and 2 was graphically integrated to obtain the amount of chlorine reacted in ten minute intervals throughout the run. These values appear in Table II. Examination of these data showed that, both for the substitution and addition reactions, the total amount of chlorine reacted without radiation increased by less than 5 percent when radiation was employed.

Total chloride analyses on the reaction mixtures gave values of 42.6 percent for run 1 and 42.4 percent for run 2. These values showed that the extent of reaction was identical for both runs.

C. Product analyses

The results obtained from product analyses on the m-xylene reaction mixtures are shown in Table III. The ranges in the theoretical percent chloride are due to the possible formation of either substitution or addition products.

The fractions obtained from the distillation of the reaction mixtures were colorless liquids. In the second fractions the liquids turned to transparent semi-solids. In the third fractions the colorless liquids became cloudy and the fourth

TABLE II. Amounts of chlorine reacted by substitution and by addition in successive time intervals during the chlorination of m-xylene at -5°C .

Type of Reaction	Run Number	Dose Rate Krep/hr.	Millimoles of Chlorine						Total
			Time Intervals, minutes						
			0-10	10-20	20-30	30-40	40-50	50-60	
Substitution	1	none	172.0	172.0	156.8	55.0	21.2	7.5	584.5
Substitution	2	60.3	164.0	164.0	160.9	76.5	33.2	13.4	612.0
Addition	1	none	42.5	46.0	57.3	154.0	146.0	48.5	494.
Addition	2	60.3	47.5	49.0	59.3	140.3	145.2	72.5	512.

TABLE III. Analytical data obtained from the distillation of chlorinated m-xylene 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	25.2	25.2	1	I	0.2	25	26.4
		25.3	2	I	0.1	25	24.0
Di	40.1-40.6	42.1	1	II	0.3	67-78	9.3
		40.2	2	II	0.1	42-65	6.7
Tri	50.4-50.9	55.5	1	III	0.2	78-91	3.5
		54.4	2	III	0.3	65-100	5.5
Tetra	57.7-58.7	60.2	1	IV	0.2	95-97	7.1
Penta	62.8-63.7	64.5	1	V	0.2	99-110	3.1
		61.4	2	IV	0.4	100-110	7.3
Hexa	67.2-68.1	-	-	-	-	-	-

* The range in values is due to the possible formation of either substitution or addition products.

fractions showed the formation of a white solid material.

No unreacted m-xylene was isolated. In both runs the most abundant fraction was related to the mono-chloro derivative of m-xylene. The formation of a di-chloro derivative was also indicated. No evidence for the presence of the tri- or tetra-chloro derivatives was found. The fractions in Table III related to these derivatives were thought to be mixtures. The last fractions from both runs indicated the formation of a penta-chloro derivative.

From these analytical data it can be seen that no significant difference in product formation exists between the irradiated and non irradiated runs.

D. Radiation yields

The kinetic data of Figures 1 and 2 and the related data in Table II show that gamma radiation had no effect on the rate of chlorination of m-xylene. Thus, G values of zero were obtained both for the substitution and addition reactions. A discussion of several factors pertinent to the calculation and interpretation of G values has been presented in an earlier report (3).

E. Discussion

Earlier work on the chlorination of a commercial xylene mixture in the presence of gamma radiation (16,17) yielded results not in agreement with the current data. The reasons for this lack of agreement in data are similar to those presented for the chlorination of naphthalene (3).

Of the three xylene isomers the meta isomer is known to be the most reactive. This fact is reflected in the current data which show a very high rate of reaction for the chlorination of m-xylene.

The results for m-xylene compare favorably with those previously obtained for mesitylene (3). The maximum substitution rate for m-xylene is lower than that obtained for mesitylene. However, the maximum addition rate for m-xylene is much higher than that obtained for mesitylene. On the basis of structure, the results obtained from the chlorination of these two compounds appear to be consistent.

II. Reaction of 1-methyl naphthalene

A. Details of the reaction

A 13 percent by weight solution of 1-methyl naphthalene in carbon tetrachloride was used in each of the experimental runs. The reactor was charged with 12.3 gm (0.086 mole) of 1-methyl naphthalene and 80 gm of carbon tetrachloride. A commercially available grade of 1-methyl naphthalene was used (Eastman Kodak P2415). Although it was originally dark amber in color, the 1-methyl naphthalene was a clear opalescent liquid after distillation.

The chlorine input flow rate used was very similar to that used for the chlorination of naphthalene (3). When the temperature of the system was at -5°C , chlorine was admitted to the reactor at this flow rate to saturate the reaction mixture. During this period the exit gases were passed through a solution

containing silver nitrate. After 5-6 minutes a precipitate of silver chloride appeared and the odor of HCl was detected. The runs were started within the next minute since the precipitate indicated the start of the reaction.

In both runs the temperature rose 14-15 degrees when chlorine was first introduced into the reactor. It was difficult to control the temperature for the first few samples but thereafter the control was good.

B. Kinetic data

The rates of reaction which were calculated for the chlorination of 1-methyl naphthalene are shown in Figures 3 and 4. Data obtained from the graphical integration of these curves are listed in Table IV.

The kinetic data presented for the substitution reaction in Figure 3 show that gamma radiation prolonged the initial reaction rate. As a result, it can be seen from Table IV that the total amount of chlorine reacted by substitution in 60 minutes in the irradiated run is about 23 percent greater than that in the non irradiated run. A maximum reaction rate plateau was observed for the substitution reaction.

From Figure 4 it is seen that the rate of chlorine addition to 1-methyl naphthalene was not affected to any extent by gamma radiation. In Table IV the total amounts of chlorine reacted by addition in 60 minutes differ by less than 2 percent. The curves for the addition reaction in Figure 4 are somewhat different from those previously encountered in this laboratory. The present data showed a reaction rate plateau in the initial

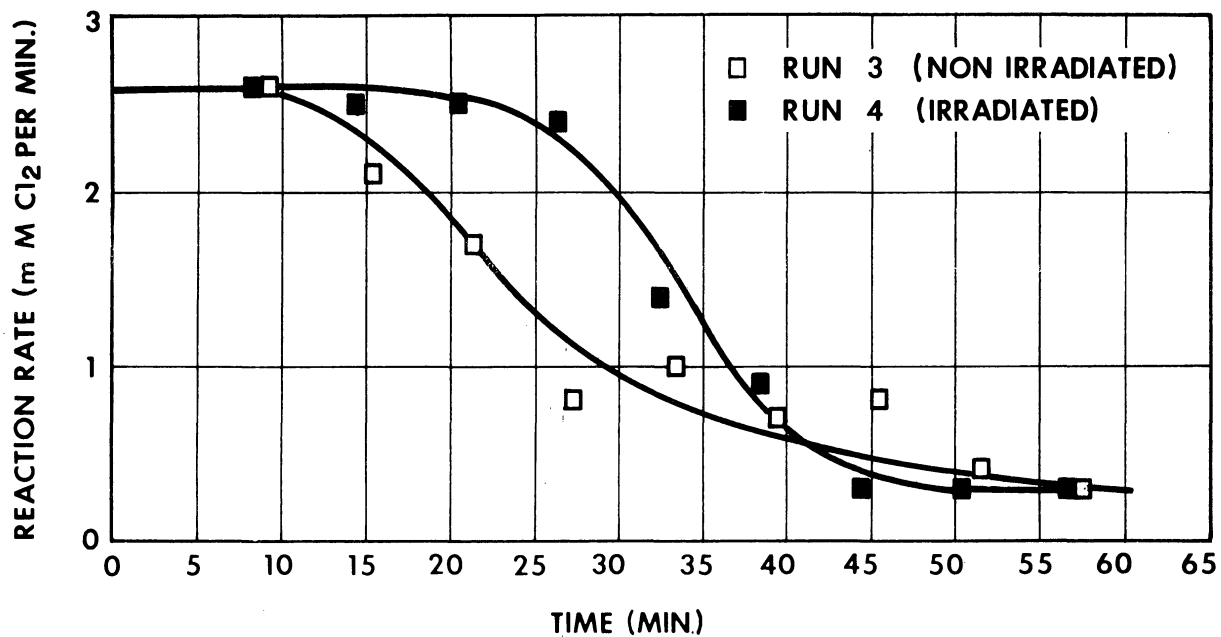


FIGURE 3. RATE OF CHLORINE SUBSTITUTION ON 1-METHYL NAPHTHALENE AT -5° C.

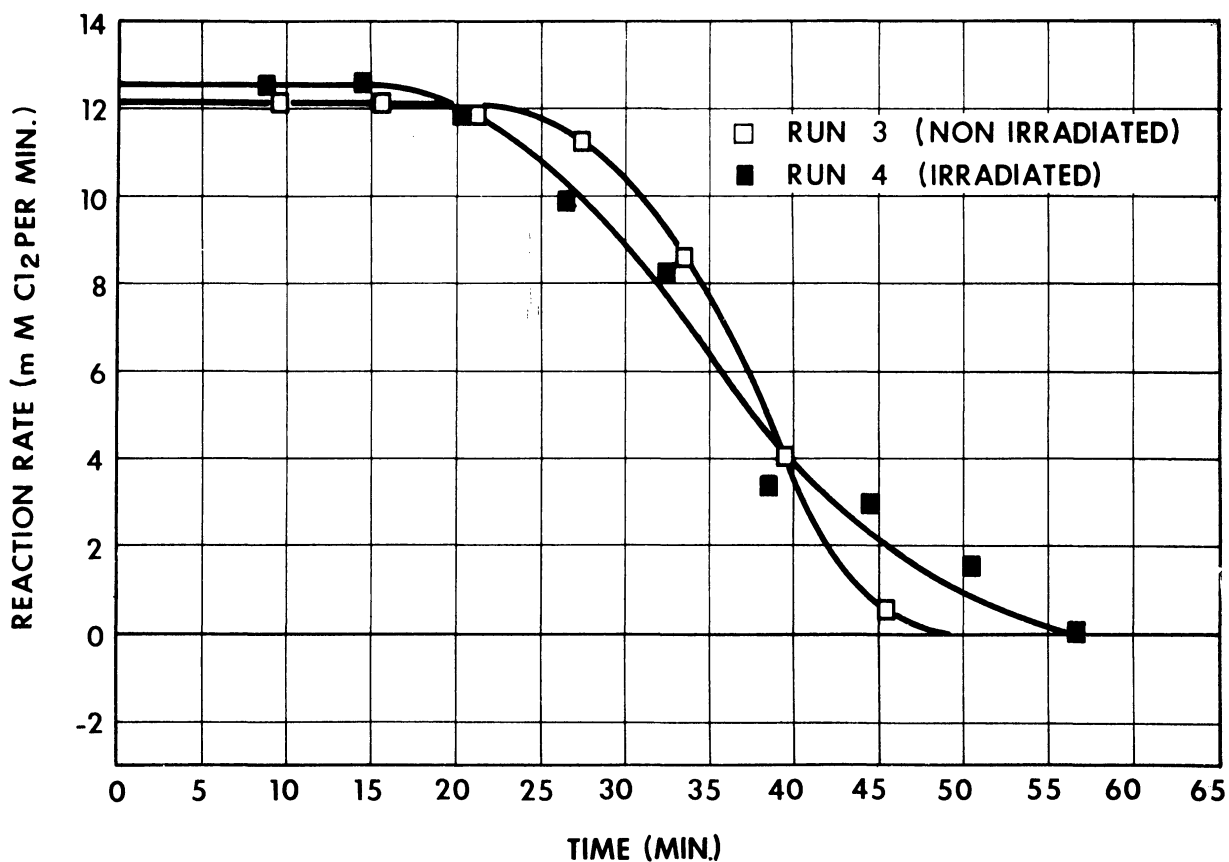


FIGURE 4. RATE OF CHLORINE ADDITION TO 1-METHYL NAPHTHALENE AT -5° C.

TABLE IV Amounts of chlorine reacted by substitution and by addition in successive time intervals during the chlorination of 1-methyl naphthalene at -5°C.

Type of Reaction	Run Number	Dose Rate Krep/hr.	Millimoles of Chlorine						Total
			Time Intervals, minutes						
			0-10	10-20	20-30	30-40	40-50	50-60	
Substitution	3	none	25.9	22.3	13.3	7.8	5.0	3.3	77.6
Substitution	4	60.3	26.0	25.8	23.5	12.9	4.1	3.0	95.3
Addition	3	none	121.0	120.5	114.0	73.5	11.5	0.0	440.5
Addition	4	60.3	125.0	124.0	106.0	64.0	24.5	3.3	446.8

part of the reaction. Previous data from other reactions showed this plateau usually occurred in the latter part of the reaction.

The effect of radiation on the extent of chlorination of 1-methyl naphthalene was indicated by total chloride analyses performed on the reaction mixtures. The values obtained were 51.1 percent for the non irradiated run and 50.4 percent for the irradiated run. Thus, it appeared that radiation had no effect on the overall reaction. However, a specific and favorable effect of gamma radiation on the substitution reaction was shown by the kinetic data.

C. Product analyses

The original reaction mixtures were dark brown in color. Only two fractions were obtained from each run after distillation. All the distillate fractions were bright yellow in color and showed the formation of a solid material on standing. Total chloride analyses were performed on these fractions and the results are listed in Table V.

The results shown in Table V allowed no definite conclusions. However, the formation of both a tri- and tetra-chloro derivative of 1-methyl naphthalene was indicated.

D. Radiation yields

Radiation yields for the reaction of chlorine with 1-methyl naphthalene have been expressed in terms of G values based on chlorine. The data of Table V was used for the calculations. For the substitution reaction, a G value of 25,100 was

TABLE V. Analytical data obtained from the distillation of chlorinated 1-methyl naphthalene 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	20.1	-	-	-	-	-	-
Di	33.3 - 33.6	-	-	-	-	-	-
Tri	43.0 - 43.3	39.4	3	I	0.4	30-147	3.7
		44.2	4	I	0.3	125-154	5.5
Tetra	50.0 - 50.7	47.1	3	II	0.3	147-151	5.5
		49.5	4	II	0.4	154-156	3.5

* The range in values is due to the possible formation of either substitution or addition products.

calculated using a 60-minute reaction time. A G value of zero was obtained for the addition reaction.

It has been recent practice to calculate G values for consecutive time intervals throughout the reaction (3,4). This approach is best adapted to a reaction which shows a reasonably high radiation yield. In the case of 1-methyl naphthalene the relatively small radiation effect is best expressed by an average G value for a specified reaction time.

E. Discussion

In naphthalene the primary substitution reaction occurs in the alpha-position which is activated by the adjacent aromatic ring. Reactions subject to steric hindrance result in substitution in the beta-position. For substitution on 1-methyl naphthalene, the 4-position is the preferential point of attack being under the directive influence of the methyl group and the adjacent aromatic ring.

In the chlorination of 1-methyl naphthalene a low rate of substitution was observed experimentally. Actually a methyl group is available for substitution as well as the 4-position. Yet, compared to naphthalene (3), only a relatively small increase in rate was observed for the substitution reaction. A reaction rate plateau was evident for the substitution reaction. This plateau has been characteristic of chlorination reactions in which the reactant contains an alkyl side chain.

Some observations on the general shape of the addition

curves obtained for 1-methyl naphthalene have already been made. The rate and extent of chlorine addition to 1-methyl naphthalene were found to be virtually unaffected by the presence of radiation. However, the addition of chlorine to naphthalene was reported to be greatly affected by gamma radiation (3). It appears that the presence of a methyl group in the 1-position of the naphthalene molecule causes a drastic decrease in the radiation yield for addition. In contrast to the decrease in radiation yield, the overall addition reaction rate for 1-methyl naphthalene was actually higher than that for naphthalene. It is worthwhile to mention that a similar effect of the methyl group on radiation yield was demonstrated for the benzene and toluene addition reactions (1,2).

In the current experiments the observed reaction rates were initially almost equal to the chlorine input rate. Thus, it is possible that higher rates of reaction may be obtained if a higher chlorine input rate were used.

III. Reaction of 2-methyl naphthalene

A. Details of the reaction

A 13 percent by weight solution of 2-methyl naphthalene in carbon tetrachloride was used in each experimental run. The sample of 2-methyl naphthalene used was Eastman Kodak white label grade number 2416. The reactor charge and general procedure were the same as that described for 1-methyl naphthalene.

In both runs the temperature rose 12-14 degrees when chlorine was introduced into the reactor and precipitation of

silver chloride was observed some 7-9 minutes later. Each run was started 10 minutes after chlorine was first admitted to the reactor.

B. Kinetic data

The kinetic data obtained for the chlorination of 2-methyl naphthalene are shown in Figures 5 and 6. The areas under these curves were graphically integrated and these data appear in Table VI.

A very low rate of substitution was observed for 2-methyl naphthalene. Figure 5 again demonstrated a plateau for the reaction rate curves. Examination of these curves showed that radiation had little effect on the substitution reaction rate. In Table VI the total amounts of chlorine reacted by substitution were found to differ by less than 6 percent.

The curves for the addition reaction in Figure 6 show that radiation had a significant effect on the reaction rate. From Table VI it can be seen that the total amount of chlorine reacted in 60 minutes for the irradiated run is about 34 percent greater than that for the non irradiated run. As in the case of 1-methyl naphthalene, a reaction rate plateau was observed during the initial part of the addition reaction. In Figure 6, the scatter of the last four data points of run 5 about the zero axis has been shown to be characteristic for a zero addition reaction rate (4).

The kinetic data for the addition reaction appear to be in agreement with the total chloride analyses performed on the

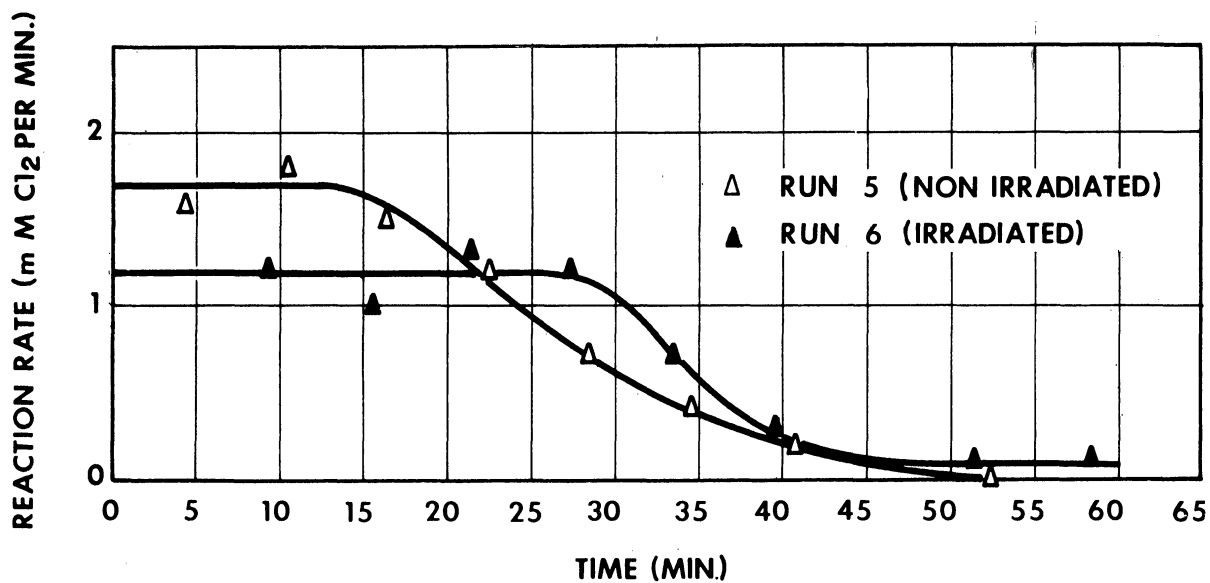


FIGURE 5. RATE OF CHLORINE SUBSTITUTION ON 2-METHYL NAPHTHALENE AT -5° C.

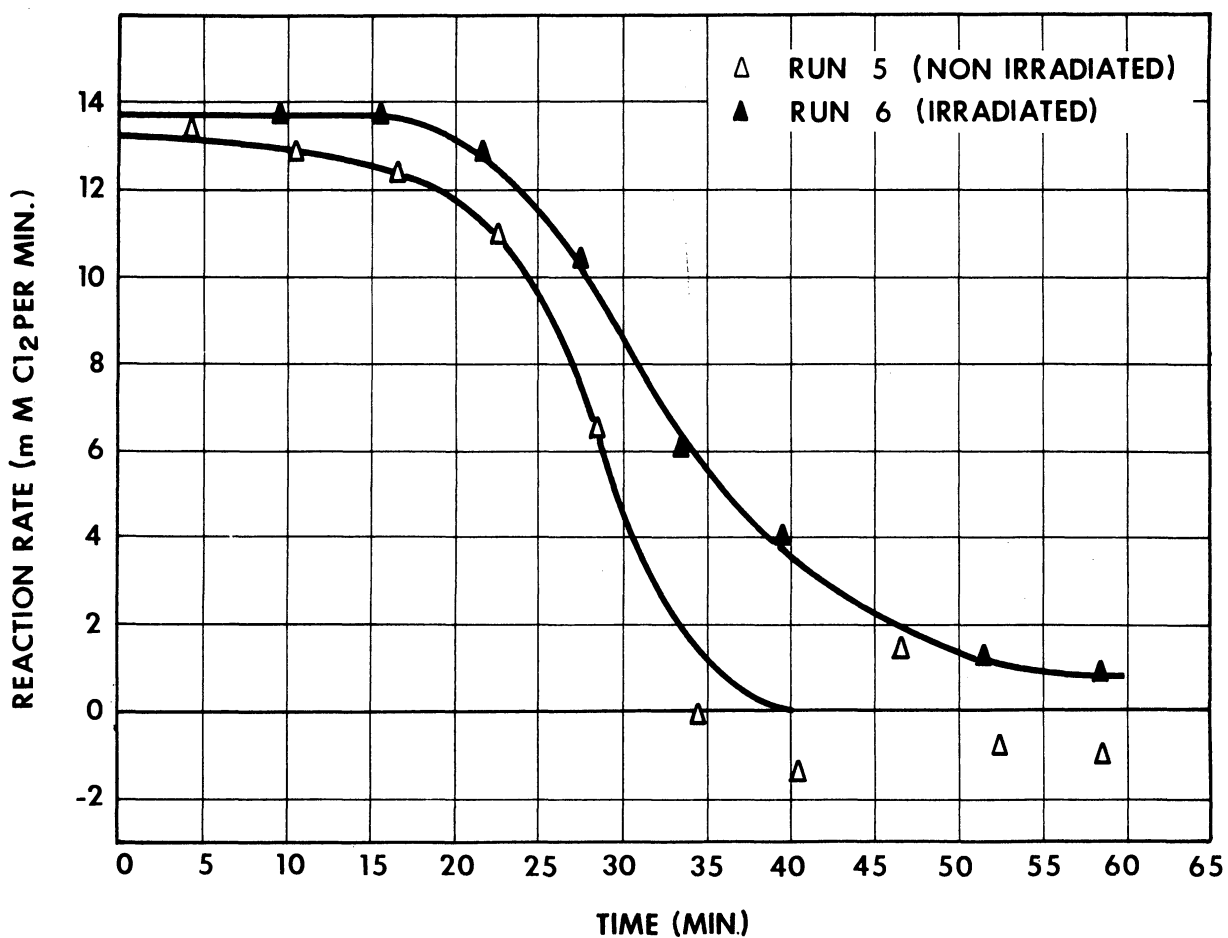


FIGURE 6. RATE OF CHLORINE ADDITION TO 2-METHYL NAPHTHALENE AT -5° C.

TABLE VI Amounts of chlorine reacted by substitution and by addition in successive time intervals during the chlorination of 2-methyl naphthalene at -5°C.

Type of Reaction	Run Number	Dose Rate Krep/hr.	Millimoles of Chlorine						Total
			Time Intervals, minutes						
			0-10	10-20	20-30	30-40	40-50	50-60	
Substitution	5	none	17.0	15.6	9.5	4.0	1.0	0.0	47.1
Substitution	6	60.3	12.0	12.0	11.6	6.5	1.5	1.0	44.6
Addition	5	none	130.0	123.6	89.5	14.2	0.0	0.0	357.3
Addition	6	60.3	137.0	136.0	113.0	58.0	24.5	10.4	478.9

reaction mixtures. These analyses indicated more product formation in the irradiated run than in the non irradiated run. The values were obtained for the total chloride content were 49.0 percent for run 5 and 53.4 percent for run 6.

C. Product analyses

The original reaction mixtures were dark tan in color. Only two distillate fractions were obtained from each run. The first fractions consisted of pale yellow liquids. The second fractions were similar in appearance but on standing these fractions became turbid as solid material started to form. The results of total chloride analyses performed on these fractions are given in Table VII.

The product fractions obtained were similar in nature to those obtained for 1-methyl naphthalene. The analytical data indicated the possible formation of both tri- and tetra-chloro derivatives of 2-methyl naphthalene. It is of interest to note that fractions related to the tri-chloro derivative were not obtained in the irradiated run.

D. Radiation yields

Radiation yields for the chlorination of 2-methyl naphthalene have been calculated from the data presented in Table VI. A G value of zero was obtained for the substitution reaction. For the addition reaction a G value of 173,000 was obtained using a 60 minute reaction time.

TABLE VII Analytical data obtained from the distillation of chlorinated 2-methyl naphthalene 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	20.1	-	-	-	-	-	-
Di	33.3 - 33.6	-	-	-	-	-	-
Tri	43.0 - 43.3	43.8	5	I	0.1	105-135	3.6
Tetra	50.0 - 50.7	51.8	5	II	0.2	131-135	3.3
		51.1	6	I	0.7	132-152	5.5
		52.0	6	II	0.7	150	2.1
Penta	56.4 - 55.7	-	-	-	-	-	-

* The range in values is due to the possible formation of either substitution or addition products.

E. Discussion

The reaction of chlorine with 1-methyl naphthalene has already been compared with that of naphthalene. This comparison can now be extended to include 2-methyl naphthalene.

It might be expected that the reactions of the two methyl substituted naphthalenes would be very similar. For example, there are the same number of positions available for substitution on both compounds. Also it is reasonable to assume that the reactivity of these positions will not differ to any great extent between the two compounds. However, the experimental results obtained for 2-methyl naphthalene are quite different from those obtained for 1-methyl naphthalene.

The most significant difference in reaction between 1-methyl naphthalene and 2-methyl naphthalene is in the radiation yields. In the chlorination of 2-methyl naphthalene, gamma radiation had a large effect on the addition reaction and very little effect on the substitution reaction. In the case of 1-methyl naphthalene this effect was reversed as only the substitution reaction was affected by radiation. Recent work on the chlorination of ethyl benzene has shown that impurities present in the reactant can cause unusual effects and can inhibit the reaction almost completely (4). Aside from considerations of reactant purity, the shift of the methyl group on naphthalene from the 1-position to the 2-position resulted in significant differences in the chlorination reaction. A resolution of these differences in reaction can only be accomplished by a thorough

study of the two reactions.

The general shapes of the reaction rate curves obtained for 1-methyl naphthalene and 2-methyl naphthalene were quite similar. Both the substitution and addition curves showed reaction rate plateaus during the early part of the reaction. For the substitution reaction, the rate of reaction of 2-methyl naphthalene was much lower than that of 1-methyl naphthalene. The overall substitution reaction, however, proceeded at a very low rate of reaction for both compounds. It was also evident that the addition reaction took place at a high reaction rate. The maximum addition reaction rate was found to be slightly greater for 2-methyl naphthalene than that for 1-methyl naphthalene.

For the addition reaction the average G value obtained for 2-methyl naphthalene was much smaller than that previously obtained for naphthalene. Thus, the comparison of the chlorination reactions of 1-methyl naphthalene and naphthalene with those of toluene and benzene already made can be extended to include 2-methyl naphthalene.

SUMMARY

1. The rates of chlorination of m-xylene, 1-methyl naphthalene, and 2-methyl naphthalene have been determined under irradiated and non irradiated conditions at -5°C .
2. For all three compounds studied, kinetic data showed that reaction with chlorine occurred both by substitution and by addition.

3. Radiation yields expressed as G values based on chlorine have been calculated for the three reactions studied.
4. At -5°C gamma radiation was found to have no effect on the rate of chlorination of m-xylene. Analytical data showed essentially no differences in product formation between the irradiated and non irradiated reactions. As a result, G values of zero were obtained for both the substitution and addition reactions.
5. Although structurally very similar, 1-methyl naphthalene and 2-methyl naphthalene exhibited different types of behavior in the presence of gamma radiation. At -5°C , both chlorination reactions were found to be favorably affected by radiation. Apart from the differences in radiation effects, the reaction rate curves and analytical data obtained for both compounds were quite similar.
6. Kinetic data showed that, during the chlorination of 1-methyl naphthalene, only the substitution reaction was affected by the presence of gamma radiation. For the substitution reaction an average G value (based on chlorine) of 25,100 was obtained for a reaction time of 60 minutes. A G value of zero was obtained for the addition reaction.
7. During the chlorination of 2-methyl naphthalene, kinetic data showed that only the addition reaction was affected by the presence of gamma radiation. For the addition reaction an average G value (based on chlorine) of 173,000 was obtained for a reaction time of 60 minutes. A G value of zero was obtained for the substitution reaction.

8. Analyses of the m-xylene reaction mixtures showed the mono-chloro derivative to be the most abundant product of reaction. The formation of the di- and penta-chloro derivatives was also indicated.
9. The results obtained from the chlorination product analyses of 1-methyl naphthalene and 2-methyl naphthalene were very similar in nature. The formation of a tri- and tetra-chloro derivative was indicated for both compounds.
10. For the chlorination reaction, the introduction of one methyl group into the naphthalene molecule gave a radiation effect similar to that found for benzene and toluene. In both aromatic systems the introduction of a methyl group resulted in a large decrease in the overall radiation yield.

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