THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THE EFFECT OF GAMMA RADIATION ON THE REACTION
OF CHLORINE WITH ETHYL BENZENE

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ACKNOWLEDGMENT

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INTRODUCTION

INTRODUCTION

The advent of the atomic energy program has stimulated many research activities to discover uses for the high-energy radiation made available directly or indirectly as the result of nuclear fission. The accumulation of large amounts of radioactive fission products from the operation of nuclear reactors has presented serious and expensive problems of contamination and storage. These fission products, which are good sources of gamma and beta radiation, are at present considered waste materials.

Six years ago, a broad program was initiated at the University of Michigan to discover uses for these fission products. As part of this program, several groups in this laboratory have been concerned with the promotion of chemical reactions by the use of radiation present in the waste fission products. These studies have been conducted using the gamma radiation obtained from cobalt-60 sources.

Of the many types of chemical reactions studied in this laboratory, this group has concerned itself with the reaction of chlorine with various aromatic hydrocarbons in the presence of gamma radiation. Benzene and toluene were among the first compounds to be chlorinated in the presence of gamma radiation (1,2). Some work on the reaction of chlorine with xylene, ethyl benzene, mesitylene, and naphthalene has also been reported (3,4). Recently, extensive studies were completed on the chlorination of mesitylene and naphthalene (5).

The chlorination of ethyl benzene has been studied extensively since the presentation of the initial data (3,4). It has been established that this reaction can be completely inhibited by impurities present in the ethyl benzene. These foreign materials present in the ethyl benzene are apparently introduced during the commercial synthesis. The results of this study are presented in two distinct parts. The first part presents data which illustrate the effect of the inhibitors on the reaction rate. The second part presents rate data, radiation yields, and product analyses for the chlorination of pure ethyl benzene.

In general, it is reported that ethyl benzene reacts with chlorine less readily than the methyl substituted benzenes and that the conditions of reaction govern the type of product obtained. Reactions carried out in bright light (6,7,8) favored chain substituted chlorides and those carried out in the presence of a carrier, such as iodine or iron, favored nuclear substituted chlorides (8,9). No reference has been found for the reaction of chlorine and ethyl benzene by addition.

Exhaustive chlorinations using both photochemical and carrier techniques in the same reaction have resulted in products which contain up to nine chlorine atoms substituted on an ethyl benzene molecule (7,8,9). Prolonged chlorination at high temperatures can result in cleavage of the ethyl benzene molecule with the formation of benzenehexachloride and assorted chloroethanes (9). Dimerization (10) and the formation of thick

resinous materials that are resistant to chlorination (7,8) appear to be the major side reactions.

From the relatively high temperatures and lengthy reaction times of the photochemical chlorinations reported in the literature, it appears that it is quite difficult to affect substitution of chlorine on the ethyl benzene molecule. The chlorinations using metallic carriers appear to proceed more readily than the photochemical chlorinations.

It may be of interest to mention that polychloro-ethyl benzenes are used as intermediates in the preparation of chloro-fluoro derivatives of ethyl benzene. These chloro-fluoro derivatives are used in the processing of uranium metal.

EXPERIMENTAL PROCEDURE

I. Preparation of Ethyl Benzene

During the experiments on the chlorination of ethyl benzene it was found that the ethyl benzene initially used contained some impurities which inhibited the reaction. After these impurities were removed, a vigorous reaction was obtained. Since it was desired to illustrate the effect of the impurities on the reaction rate, it became necessary to specify how the two reactants had been prepared for use.

A. Distilled Ethyl Benzene (I)

A commercially available grade of ethyl benzene was used. (Eastman Kodak 719). The reagent was dried over calcium chloride and silica gel and subsequently distilled twice. Only

the middle 50 percent of the distillate was collected for use. The distilled ethyl benzene was completely colorless and was designated "ethyl benzene (I)".

The commercial ethyl benzene was initially pale yellow in color. After distillation, the discarded ethyl benzene was distinctly darker yellow in color and had an astringent odor.

B. Sodium-Purified Ethyl Benzene (II)

Distilled ethyl benzene (I) from the first purification procedure was treated with freshly-cut metallic sodium. Within minutes a flocculation occurred in the solution. A bright yellow material was noted to be adsorbed on the surface of the sodium shavings. This was accompanied by the formation of a white flocculent material which slowly settled to the bottom of the solution. Evolution of gas bubbles was evident during the precipitation.

After five hours the ethyl benzene solution was filtered. The flocculated material was very gelatinous in texture and had a pleasant aromatic odor.

The filtered ethyl benzene (I) solution was treated with several portions of metallic sodium during the course of one week. When removed, each portion of sodium except the last had some bright yellow material adsorbed on the surface. The ethyl benzene was distilled when no further reaction with metallic sodium was apparent. As before only the middle portion of the distillate was collected for use. This constituted "ethyl benzene (II)".

There was no noticeable difference in the color or odor of ethyl benzene (I) and (II). Infrared spectrograms of these two samples of ethyl benzene were identical although the sodium-purified sample contained much less impurity than the sample that was merely distilled.

II. General Method

A complete description of the equipment and procedure employed in the chlorination studies has been presented in a recent report (5).

The rates of reaction of chlorine with ethyl benzene were calculated by an overall chlorine material balance on the reacting system.

The chlorine inlet gas flow rate was measured by a calibrated rotameter-type flow meter. Samples of the exit gases from the reactor were absorbed in 0.2 N sodium arsenite in 3 N potassium hydroxide solution. The amount of unreacted chlorine present in each sample of the exit gases was determined by titration with ceric sulfate. The amount of chloride ion present was determined by the Volhard titration method.

A thermocouple recorder-controller was used to control the temperature of the reacting system. The radiation dose rate was measured by ferrous sulfate dosimetry (11).

The reaction products were fractionated in a simple vacuum distillation unit. The total chloride content of each of the resultant distillate fractions was determined by chemical methods.

RESULTS

I. <u>Reaction of Chlorine with Distilled Ethyl Benzene (I)</u>

   A. Reaction Conditions

   For all runs the reactor was charged with 60 ml (0.49 mole) of ethyl benzene (I). After the reactor had attained the operating temperature, chlorine gas was admitted at a rapid rate in order to saturate the ethyl benzene (I). During this period no odor of chlorine or HCl was noted in the exit gas lines. After saturation was completed and the temperature became steady the gamma source was raised and chlorine gas was admitted at a constant flow meter setting. This was taken as zero time. The data points shown represent the middle of the sample absorption period.

   The experimental conditions used are summarized in Table I. Run 6 had data points taken at two different chlorine inlet rates. The data show that this change in flow rate had no effect on the reaction.

   From Table I it can be seen that the chlorine inlet rate showed a slight variation in most of the runs. However, during any given sample of a run, the chlorine inlet rate was constant at some value in the range shown in the last column of Table I.

   B. The Substitution Reaction

   The kinetic data for the reaction of ethyl benzene (I) and chlorine by substitution are shown in Figures 1, 2, and 3. Virtually little difference exists in the results obtained at the

FIGURE 1. RATE OF CHLORINE SUBSTITUTION ON ETHYL BENZENE (I)
AT 60° C. (RUN 1)

FIGURE 2. RATE OF CHLORINE SUBSTITUTION ON ETHYL BENZENE (I)
AT -5° C.

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FIGURE 3. RATE OF CHLORINE SUBSTITUTION ON ETHYL BENZINE (I) AT -25° C.

The figure shows a plot with axes:
- Y-axis (vertical): REACTION RATE (m M Cl₂ PER MIN.), ranging from -1 to 3
- X-axis (horizontal): TIME (MIN.), ranging from 0 to 85

Legend:
- ○ RUN 6 (NON IRRADIATED)
- □ RUN 7 (NON IRRADIATED)
- △ RUN 8 (NON IRRADIATED)
- ● RUN 9 (IRRADIATED)

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TABLE I.   Summary of Experimental Conditions used in the Chlorination of Ethyl Benzene (I).

Run No.	Reaction Temp. °C	Dose Rate Krep/hr.	Sample Time min.	Run Time min.	Chlorine Inlet Rate mM/min.
1	60	31.5	5	65	13.2
2	-5	none	10	84	12.2 - 13.1
3	-5	none	10	101	12.5 - 13.1
4	-5	13.2	10	96	13.3 - 14.2
5	-5	13.2	10	96	13.1
6	-25	none	5 4	83	13.9 - 14.0 21.7 - 21.8
7	-25	none	5	82	14.1
8	-25	none	5	88	14.0 - 14.1
9	-25	60.3	5	65	14.3 - 14.6

three different temperatures and radiation dose rates.

Examination of the data revealed that gamma radiation had no measurable effect on the substitution reaction.

C.   The Addition Reaction

Figures 4, 5, and 6 illustrate the rates of addition of chlorine to ethyl benzene (I) at three temperatures.

From Figure 4 it can be concluded that no reaction by addition occurs at 60°C.

Data from both the irradiated and non irradiated runs at -5°C showed random scatter about the zero axis. No finite rates of addition could be determined from the data shown in Figure 5.
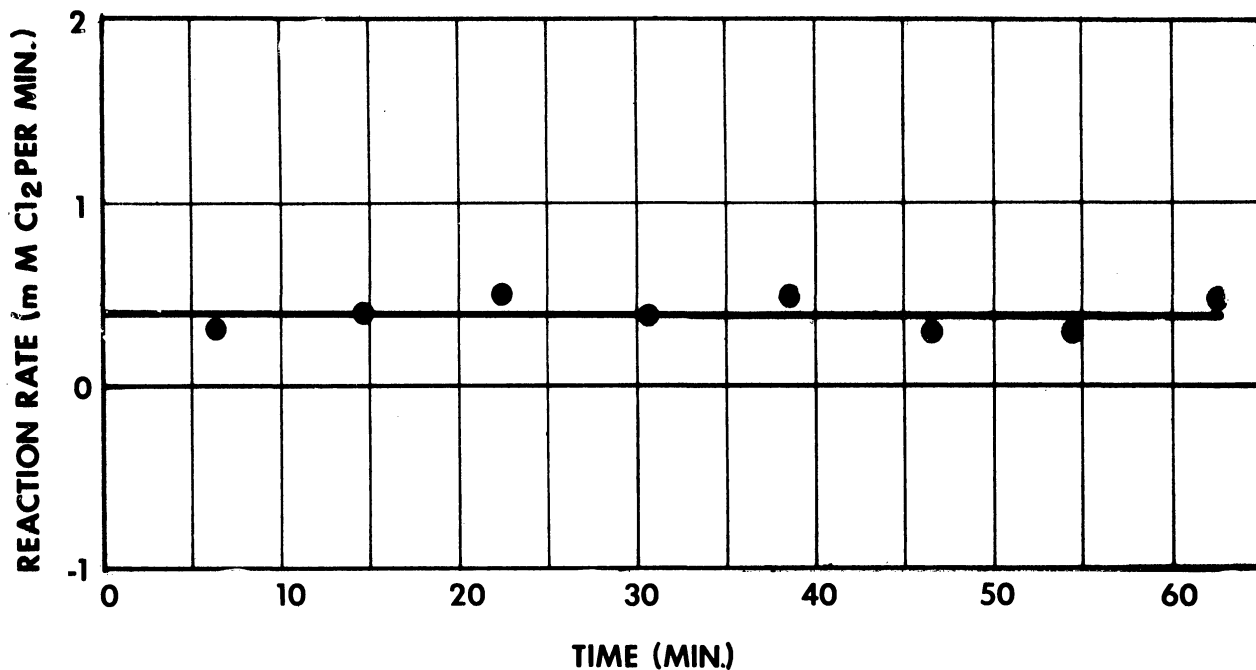
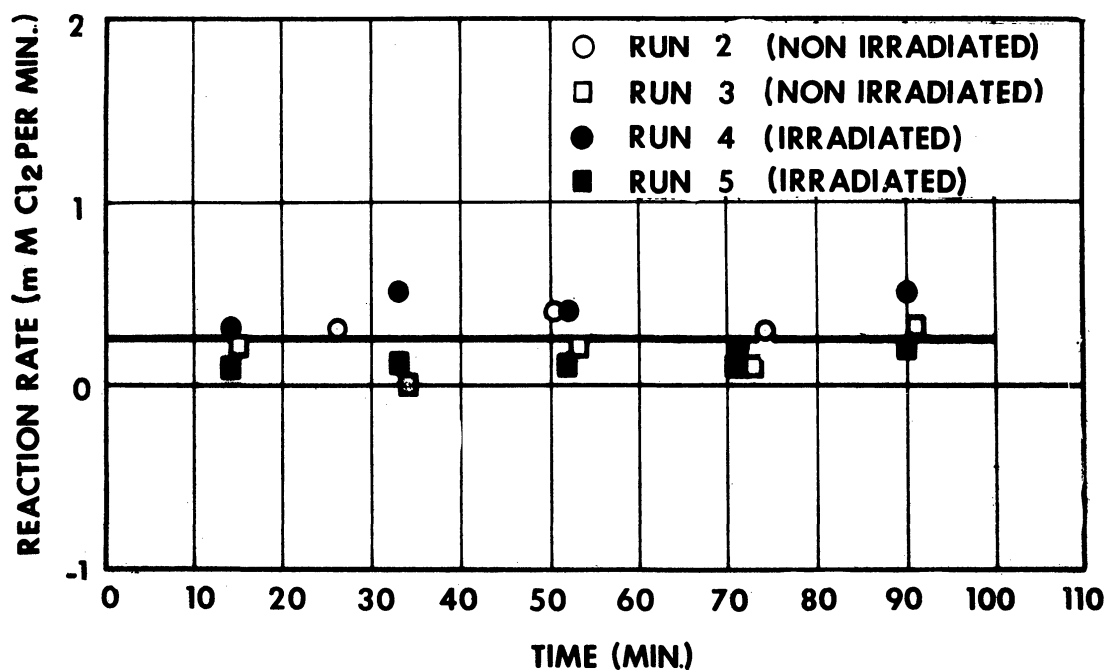FIGURE 4. RATE OF CHLORINE ADDITION TO ETHYL BENZENE (I)
AT 60° C. (RUN 1)

FIGURE 5. RATE OF CHLORINE ADDITION TO ETHYL BENZENE (I)
AT -5° C.

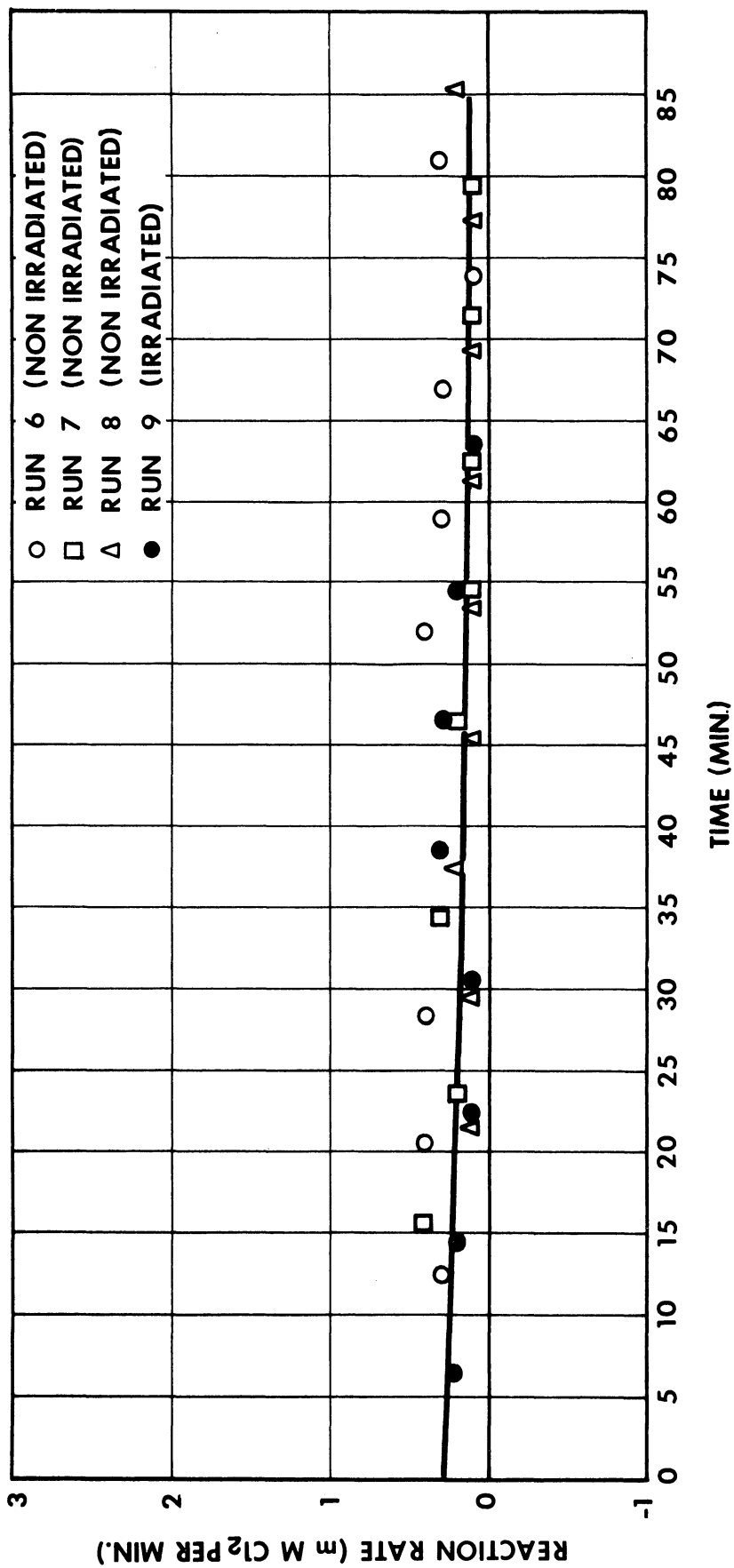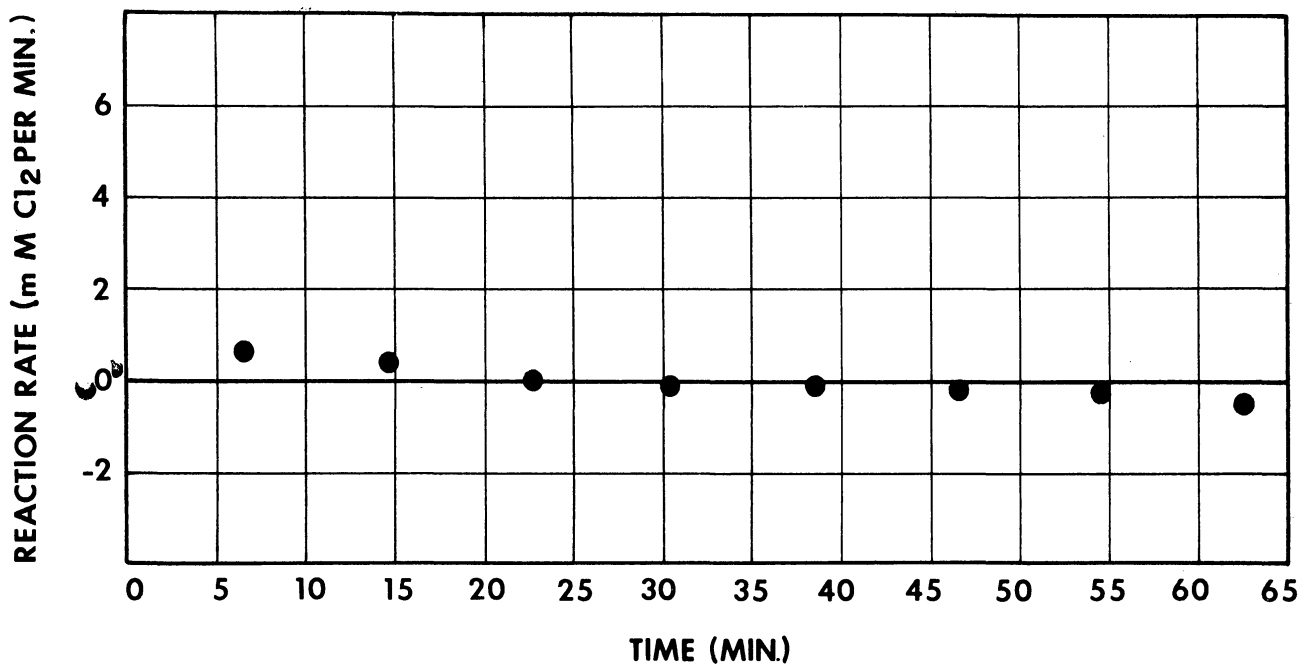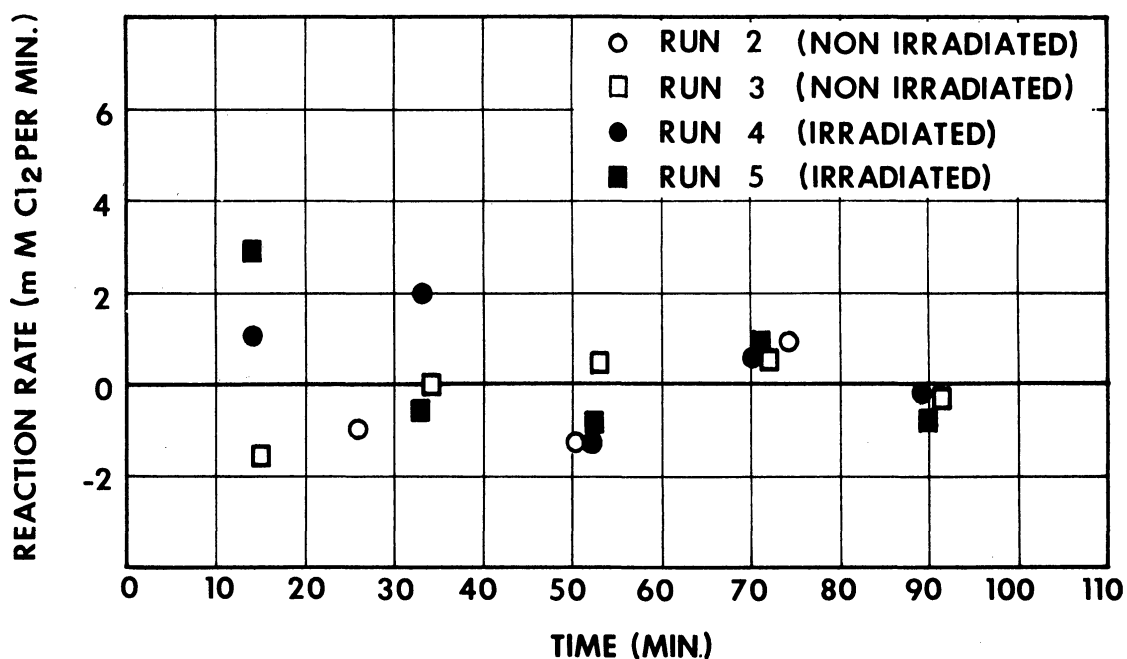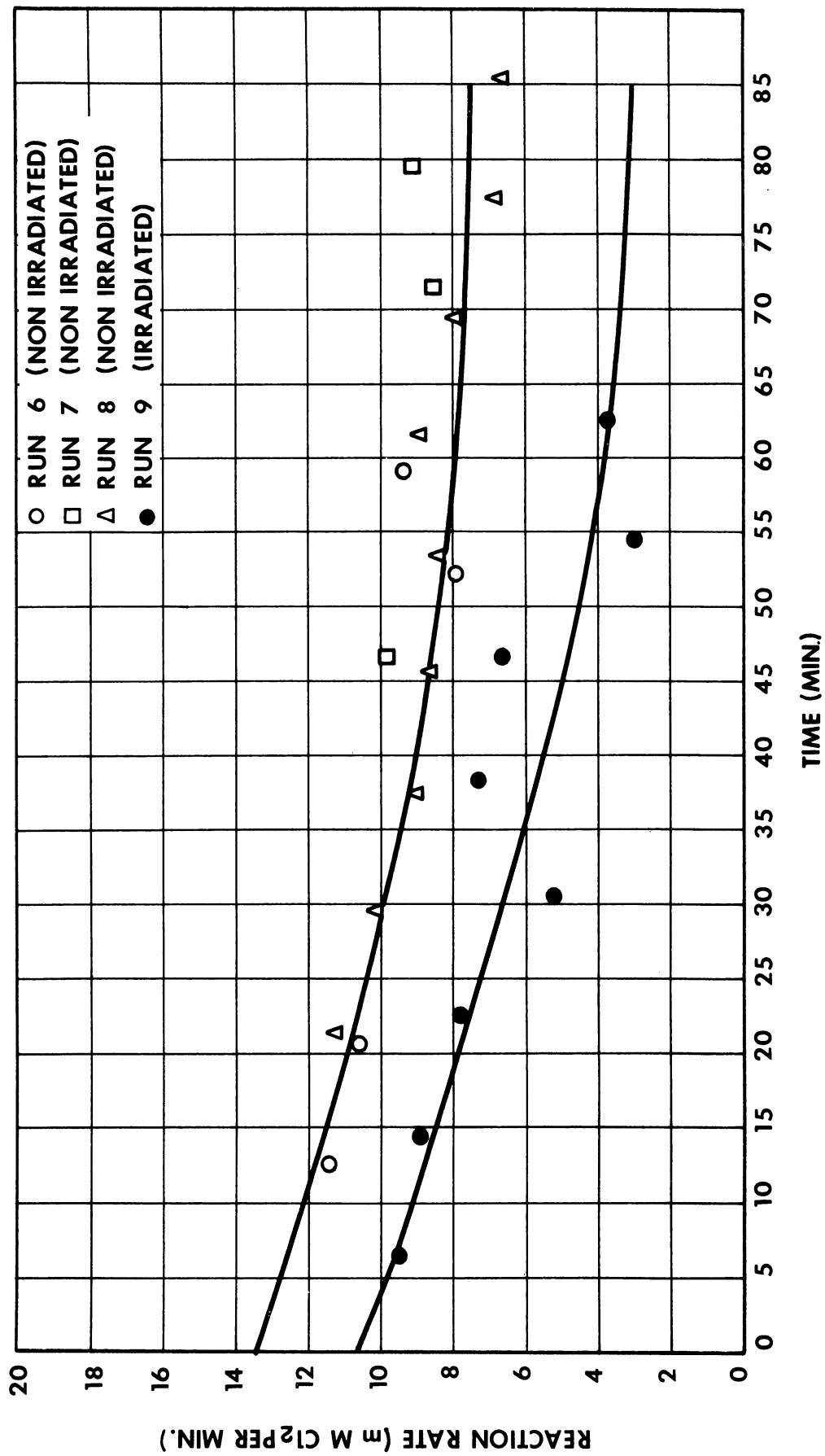FIGURE 6. RATE OF CHLORINE ADDITION TO ETHYL BENZENE (I) AT -25° C.

TIME (MIN.)

REACTION RATE (m M Cl₂ PER MIN.)

RUN 6 (NON IRRADIATED)
RUN 7 (NON IRRADIATED)
RUN 8 (NON IRRADIATED)
RUN 9 (IRRADIATED)

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The results of the four runs at -25°C showed an unusual effect. Figure 6 showed that gamma radiation had an inhibiting effect on the addition of chlorine to ethyl benzene (I). The reaction rate under irradiation was significantly lower than that without radiation. This anomalous behavior was one of several factors which eventually led to the discovery and subsequent removal of impurities present in the ethyl benzene (I).

D. Product Analyses

The extent of reaction that had occurred in each of the experimental runs could easily be determined by performing a total chloride analysis on the reaction mixtures. Table II showed that very little difference existed in the extent of reaction in the runs conducted with ethyl benzene (I). The relatively high values obtained for runs 2, 3, 4, and 5 in Table II were thought to be due to prolonged contact with dissolved chlorine gas prior to analysis.

TABLE II. The Percentage of Total Chloride Present in the Original Ethyl Benzene (I) Reaction Mixtures.

Run No.	Reaction Temp. °C	Dose Rate Krep/hr.	% Total Chloride in Reaction Mixture
1	60	31.5	3.4
2	-5	none	16.2
3	-5	none	18.4
4	-5	13.2	13.6
5	-5	13.2	13.4
6	-25	none	4.2
7	-25	none	-
8	-25	none	-
9	-25	60.3	9.6

The reaction mixtures from the chlorination of ethyl benzene (I) were distilled under reduced pressure and the total chloride content of each distillate fraction was determined. Typical data obtained from the distillations at -5°C and -25°C are illustrated in Table III.

A large amount of unreacted ethyl benzene (I) was found to be present in each reaction mixture. The fractions containing significant amounts of total chloride were of varying viscosities and were yellow in color. The presence of a mono-chloro derivative was strongly indicated. It is thought that the other fractions listed in Table III are mixtures of the mono-chloro derivative and some much higher chloro derivative, possibly the tetrachloride compound.

At -5°C the experimental runs showed literally no difference in product composition. Only two distinct fractions were isolated from each run.

Some differences in product composition was noted for the runs at -25°C. For example, in run 8, the last distilled fraction contained only 3.6 percent by weight of total chloride. This indicated no product formation for the non irradiated run. The distillate fractions isolated from run 9 showed a high total chloride content.

These analytical data did not substantiate the kinetic data which showed a higher reaction rate for the non irradiated runs than for the irradiated run.

TABLE III. Typical Data Obtained from the Distillation of Chlorinated Ethyl Benzene (I) 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.
Mono	25.2	25.0	2	I	22-26	61-74	3.5
		25.1	3	I	32-36	60-75	4.0
		25.5	4	I	22-24	68-72	2.5
Di	40.1-40.6	-	-	-	-	-	-
Tri	50.4-50.9	54.3	2	II	22	80-152	3.5
		53.7	3	II	28-32	105-152	4.3
		55.5	4	II	22	103-153	2.5
		54.3	9	I	0.3	74-86	0.7
Tetra	57.7-58.7	57.3	9	II	0.3	85-90	1.0

II. <u>Reaction of Chlorine with Sodium-Purified Ethyl Benzene (II)</u>

    A. Reaction Conditions

        The runs employing ethyl benzene (II) as a reactant were set up in the same manner as that previously described for ethyl benzene (I). During the course of saturating the reactor with chlorine there was no evidence of reaction by substitution. During saturation, the exit gas stream was directed through a solution containing silver nitrate. No precipitate of silver chloride was observed until chlorine gas was actually visible in the exit lines.

        The chlorination of ethyl benzene (II) was conducted at the two temperatures for which extensive data was available using ethyl benzene (I). A summary of the experimental conditions is given in Table IV.

TABLE IV. Summary of Experimental Conditions
Used in the Chlorination of Ethyl
Benzene (II).

Run No.	Reaction Temp. °C	Dose Rate Krep/hr.	Sample Time min.	Run Time min.	Chlorine Inlet Rate mM/min.
10	-5	none	4	76	14.8-14.9
11	-5	60.3	4	75	14.3-14.6
12	-25	none	4	76	14.7-14.9
13	-25	60.3	4	75	14.6-14.9
14	-25	60.3	5	97	14.1

        The runs at -25°C were extremely hard to control. The chief difficulty was the large amount of chlorine dissolved in the ethyl benzene (II) during the saturation period. The solubility of chlorine in ethyl benzene (II) was measured at two

temperatures using a calibrated flow meter. The solubility values
obtained were as follows: 0.51 gm per ml at -5°C; 1.80 gm per ml
at -25°C. This solubility data indicates that the best possible
temperature control was mandatory for the runs at -25°C. Even
a slight variation in temperature would make a material balance
impossible.

In all runs using ethyl benzene (II), a temperature
rise was observed when chlorine was first admitted to the reactor.
This rise was 2 degrees for the runs at -5°C. For the runs at
-25°C this temperature rise varied from 6 to 15 degrees.

In the irradiated runs using ethyl benzene (II) a sharp
temperature rise was observed when the gamma source was raised
from its storage well. For run 14 this second temperature rise
was 2 degrees. A rise of 4 degrees was noted in runs 11 and 13.
The raising of the gamma source was also accompanied by violent
gas evolution from the reactor. At -25°C this gas evolution
disturbed the equilibrium to the extent that no data points were
available for the early part of the reaction.

The second temperature rise and sudden gas evolution
from the reactor were not observed for the non irradiated runs.
These observations indicated that gamma radiation had a great
effect on the reaction. This conclusion was later confirmed
both by the kinetic and analytical data.

B. The Substitution Reaction

Figures 7 and 8 illustrate the effect of radiation on
the rate of chlorine substitution on ethyl benzene (II).
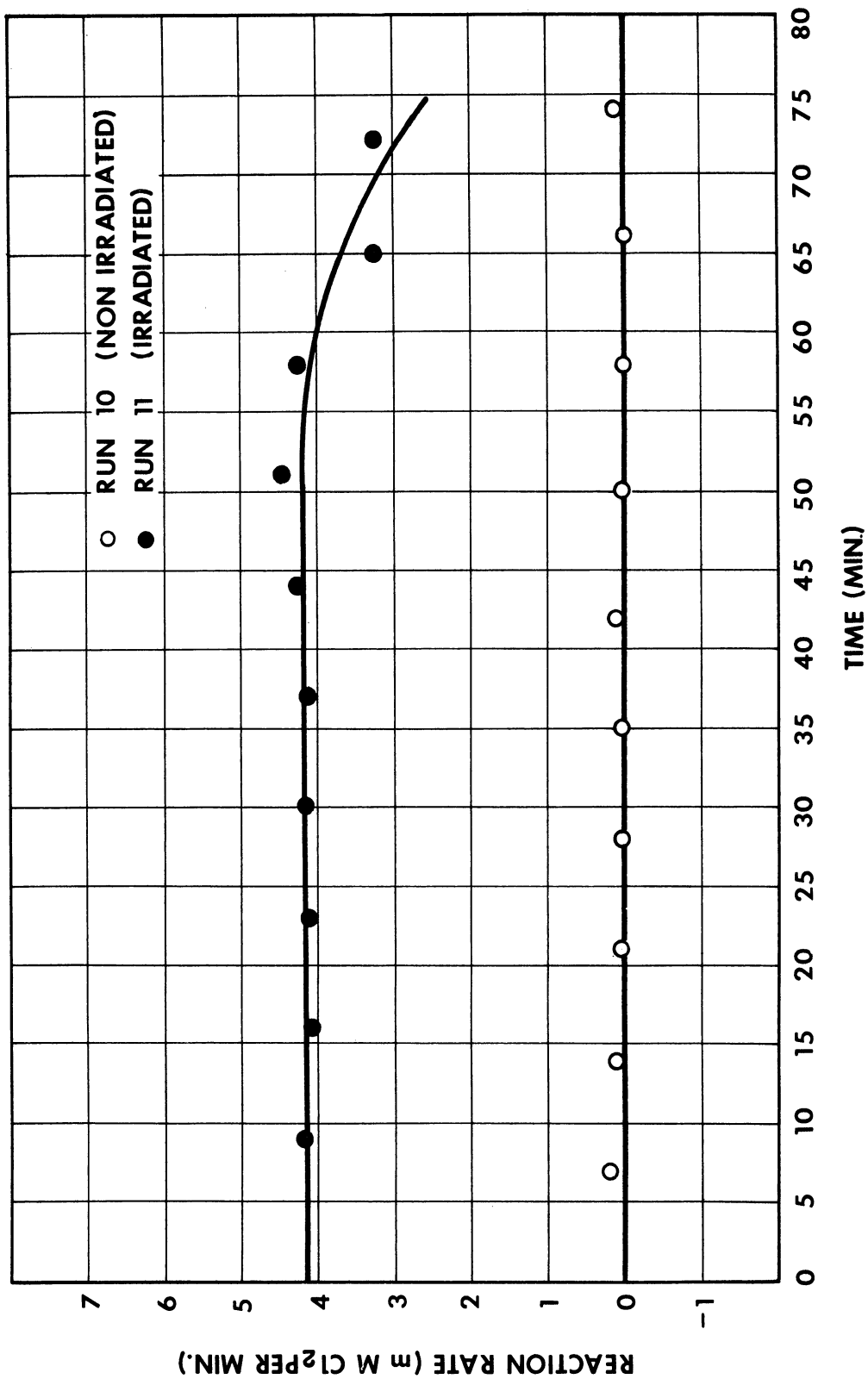
FIGURE 7. RATE OF CHLORINE SUBSTITUTION ON ETHYL BENZENE (II) AT -5° C.

The graph shows REACTION RATE (m M Cl$_2$ PER MIN.) on the vertical axis (from -1 to 7) versus TIME (MIN.) on the horizontal axis (from 0 to 80).

Legend:
- ○ RUN 10 (NON IRRADIATED)
- ● RUN 11 (IRRADIATED)

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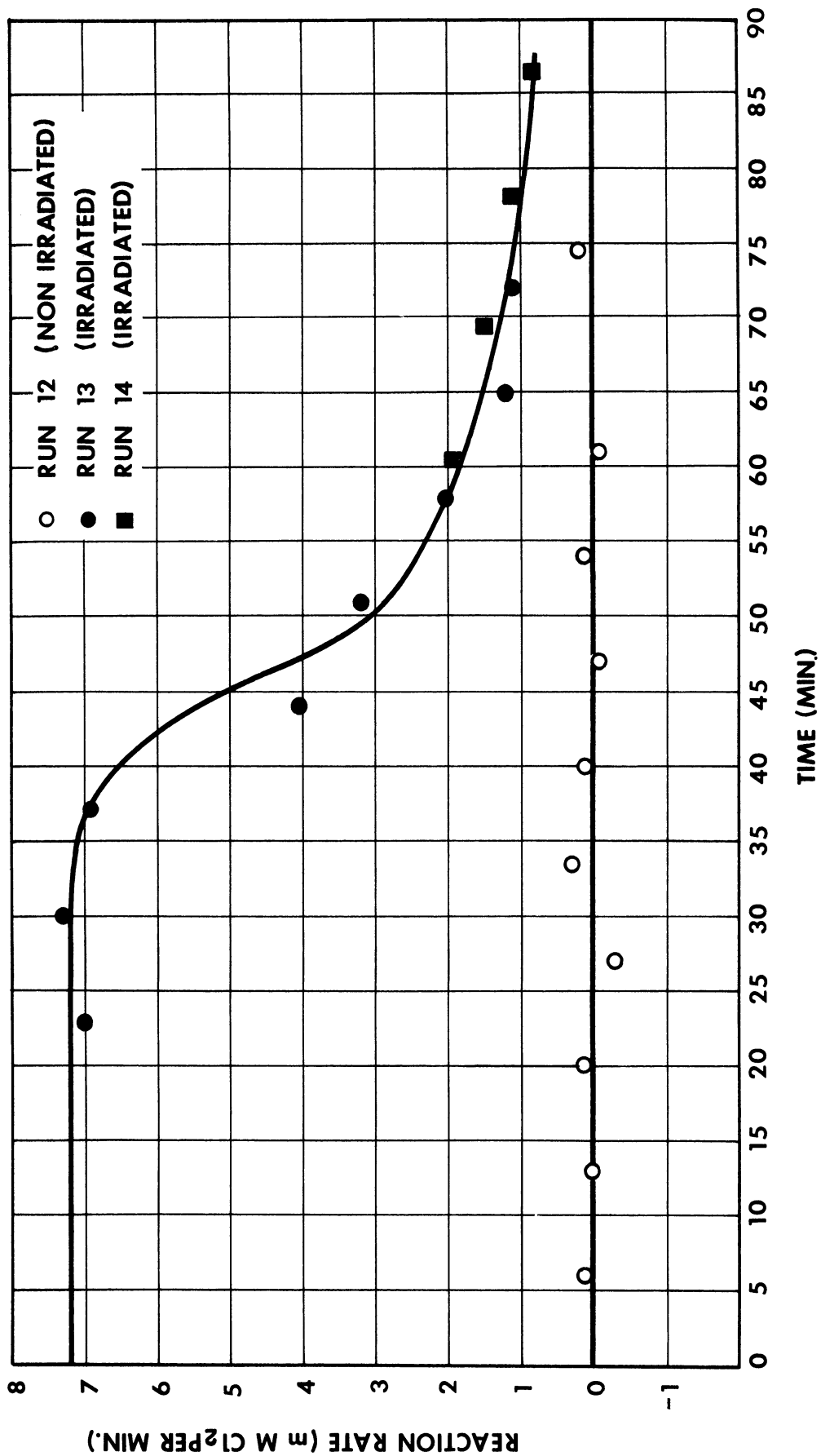
FIGURE 8. RATE OF CHLORINE SUBSTITUTION ON ETHYL BENZENE (II) AT -25° C.

TIME (MIN.)

REACTION RATE (m M Cl$_2$ PER MIN.)

RUN 12 (NON IRRADIATED)
RUN 13 (IRRADIATED)
RUN 14 (IRRADIATED)

There was no reaction by substitution in the non irradiated runs at -5°C and -25°C. However, a significant amount of substitution did occur under irradiation at both temperatures. The irradiated curves of Figures 7 and 8 were characterized by plateaus during the early part of the reaction. In this plateau region, the reaction rate at -25°C was about 1.7 times larger than that at -5°C. Examination of the areas under the plateau regions of the curves reveals that, at both temperatures, the reaction rate starts to decrease at the point where the ratio of the total moles of chlorine reacted by substitution to the total moles of ethyl benzene (II) charged is 1 to 2.

The substitution curves were graphically integrated to obtain the amount of chlorine reacted in ten minute intervals. This data is presented in Table V and will be used in the calculation of radiation yields.

C. The Addition Reaction

Kinetic data for the addition of chlorine to ethyl benzene (II) at -5°C and -25°C are shown in Figures 9 and 10.

Smooth reaction rate curves were obtained under irradiation. However, comparison of the non irradiated data points of Figures 7 and 8 showed a distinct scatter about the zero axis. Further, both non irradiated runs showed almost a sinusoidal variation about this axis. This observation indicated a possible temperature variation in the reactor. The effect of such a temperature variation would be an alternate evolution of dissolved chlorine followed by solution of the input chlorine.

TABLE V. Millimoles of Chlorine Reacted by Substitution in Successive Time
Intervals During the Chlorination of Ethyl Benzene (II).

Reaction Temp. °C	Dose Rate Krep/hr.	Millimoles of Chlorine Time Intervals, minutes							Total
		0-10	10-20	20-30	30-40	40-50	50-60	60-70	
-5	none	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
-5	60.3	41.4	41.4	41.4	41.3	41.2	40.9	36.0	283.6
-25	none	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
-25	60.3	72.0	72.0	71.8	69.7	48.0	24.5	15.4	373.4
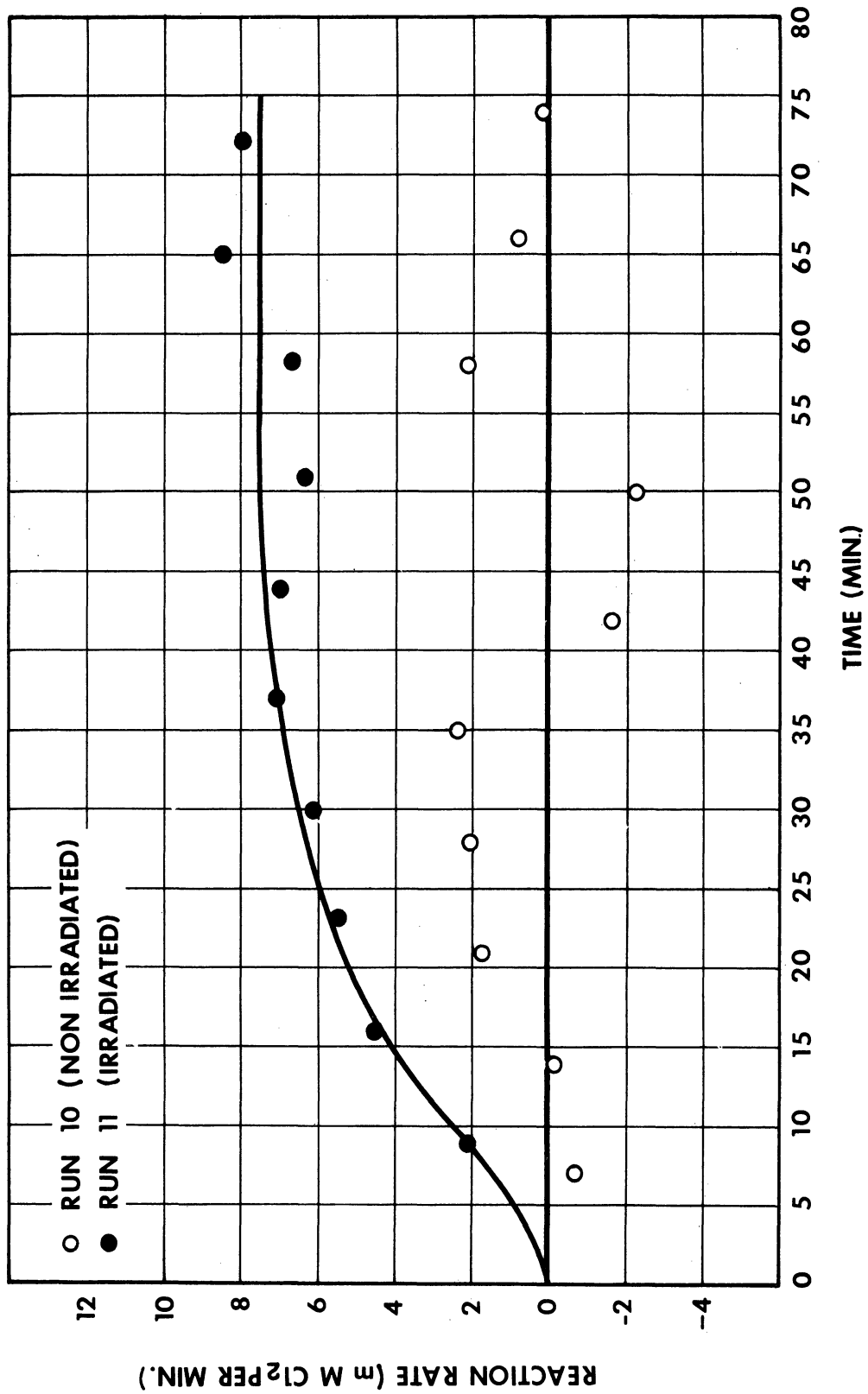
FIGURE 9. RATE OF CHLORINE ADDITION TO ETHYL BENZENE (II) AT -5° C.

Legend (on plot):
o RUN 10 (NON IRRADIATED)
● RUN 11 (IRRADIATED)

X-axis: TIME (MIN.)
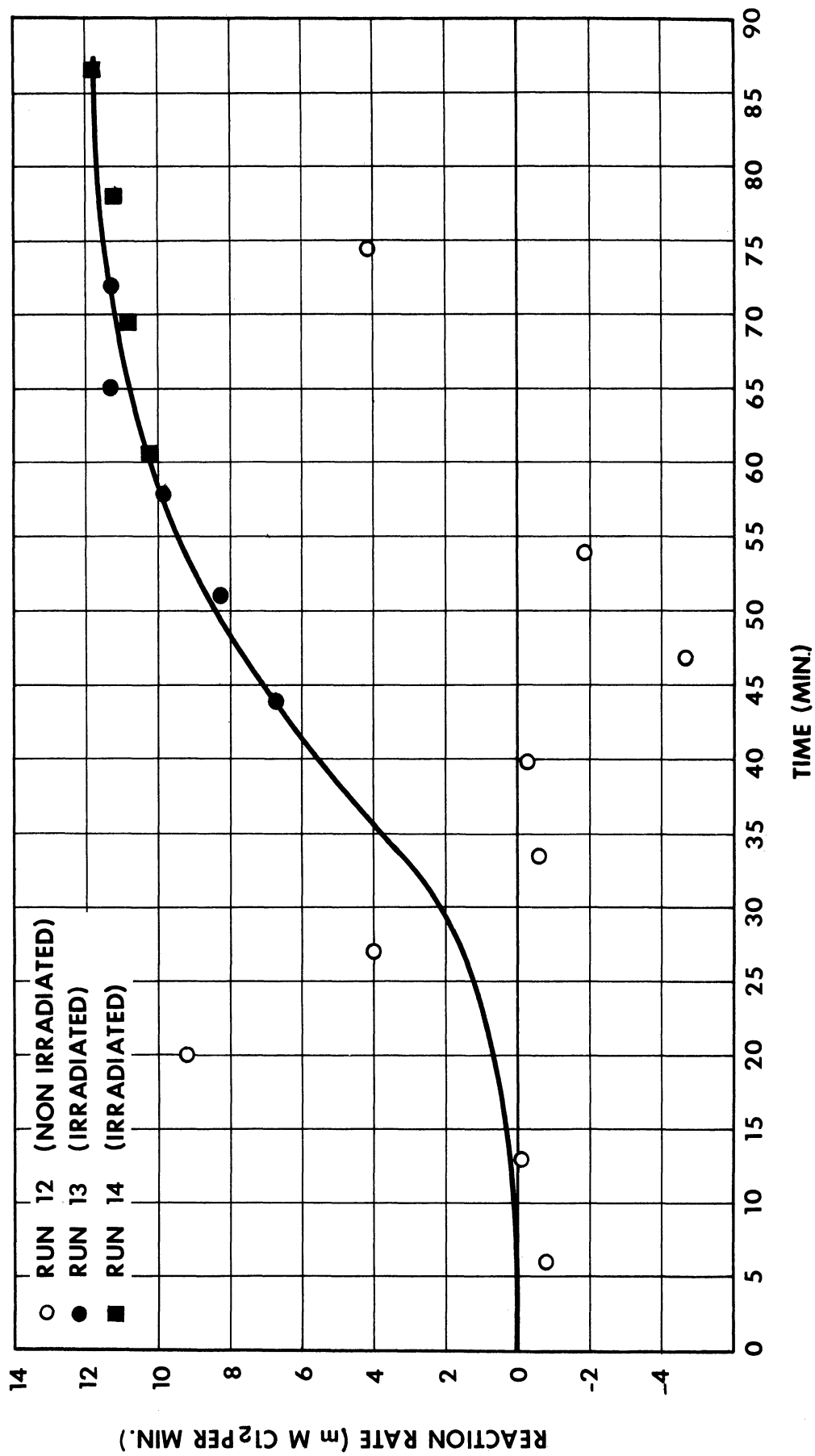Y-axis: REACTION RATE (m M Cl₂ PER MIN.)

FIGURE 10. RATE OF CHLORINE ADDITION TO ETHYL BENZENE (II) AT -25° C.

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The end result would be a sine curve in the chlorine material
balance. In the event that no reaction occurs this sine curve
would be about the zero axis.

The non irradiated runs were established to represent
a zero reaction rate. The major evidence for this conclusion was
obtained from total chloride analyses on the original reaction
mixtures. These data are present in Table VI. For example, in
run 10 the reacted ethyl benzene (II) contained 3.2 percent by
weight of total chloride. This percentage is equivalent to a
constant addition reaction rate of 0.3 mM chlorine per minute
during the entire .76 minutes of the run. This value has been
considered negligible in comparison with the irradiated reaction
rates and therefore has been designated as zero.

TABLE VI. The Percentage of Total Chloride Present in
the Original Ethyl Benzene (II) Reaction Mixtures.

Run No.	Reaction Temp. °C	Dose Rate Krep/hr.	% Total Chloride in Reaction Mixtures
10	-5	none	3.2
11	-5	60.3	53.3
12	-25	none	3.0
13	-25	60.3	58.5
14	-25	60.3	58.6

All irradiated reaction mixtures yielded high percent-
ages of total chloride. These values substantiated the conclu-
sions drawn from the kinetic data.

The irradiated reaction rate curves of Figures 9 and 10 were quite similar in appearance. A period of induction occurred for the addition reaction at both temperatures. During this period the reaction rate was seen to increase to a maximum value. This maximum reaction rate plateau was attained after 50 minutes at -5°C and after 80 minutes at -25°C. In this plateau region the reaction rate at -25°C was 1.6 times larger than that at -5°C.

The difference in length of the induction periods at the two temperatures appeared to be related to the corresponding rates of substitution. It is possible that the substitution reaction may occur preferentially. At -5°C the addition reaction rate had already exceeded the substitution reaction rate at the 16 minute mark. However, at this temperature the substitution reaction rate was fairly low. At -25°C the rate of substitution was quite high and here the addition reaction rate did not surpass the maximum substitution rate until the rate of substitution had fallen off by some 39 percent. This occurred around the 46 minute mark.

The integration data of Table VII showed how the total amount of chlorine reacted per time unit increases with reaction time. This data will be used in the calculation of radiation yields.

D. Product Analyses

All reaction mixtures from the chlorination of ethyl benzene (II) were distilled under 0.2-0.5 mm. Hg. pressure.

TABLE VII. Millimoles of Chlorine Reacted by Addition in Successive Time Intervals During the Chlorination of Ethyl Benzene (II).

Reaction Temp. °C	Dose Rate Krep/hr.	Millimoles of Chlorine Time Intervals, minutes								Total
		0-10	10-20	20-30	30-40	40-50	50-60	60-70	
-5	none	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
-5	60.3	9.6	39.0	58.2	68.4	73.0	74.6	74.7	397.5
-25	none	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
-25	60.3	1.0	3.5	12.0	37.0	69.0	93.0	106.5	322.0

Samples of the reaction mixtures were taken for total chloride analysis after any dissolved chlorine had been removed from the reaction mixture but prior to the actual distillation.

The distillate fractions obtained from the non irradiated runs were similar in number and appearance. Actually no product fractions were isolated. The fractions consisted of unreacted ethyl benzene (II) and most of them contained less than one percent by weight of total chloride. The last fraction in run 10 was 1 ml in volume and contained 8.5 percent total chloride. In view of these results it was concluded that no reaction of chlorine with ethyl benzene (II) had occurred in the non irradiated experiments.

The distillate fractions from the irradiated runs yielded no unreacted ethyl benzene (II). All fractions were colorless liquids of varying viscosities. The high boiling fractions were the most viscous. Table VIII contains all the data available for the distillation of the irradiated reaction mixtures. The range in the theoretical percent chloride column of this table is due to the possible formation of either substitution or addition products.

The data in Table VIII indicated the formation of a mono-chloro derivative of ethyl benzene (II). No distinct fraction corresponding to the di- or tri-chloro derivatives was obtained. Also, only a few fractions were obtained which were related to the tetra- and penta-chloro derivatives. The majority of the distilled fractions corresponded to the hexa-chloro derivative of ethyl benzene (II). In all probability this was the

TABLE VIII. Analytical Data Obtained from the Distillation of Chlorinated Ethyl Benzene (II) 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	23.6	11	I	0.5	27	11.5
		27.2	11	II	0.5	30	2.2
		25.7	13	I	0.5	23	0.2
		26.6	13	II	0.3	27-28	9.6
		30.4	13	III	0.3	29-30	1.3
		26.4	14	I	0.2	28	8.6
		30.4	14	II	0.3	28	1.0
Di	40.1-40.6	—	—	—	—	—	—
Tri	50.4-50.9	54.0	13	IV	0.3	42-85	4.2
		55.1	14	III	0.2	45-111	7.0
Tetra	57.7-58.7	58.7	11	III	0.5	90-112	11.0
		58.3	13	V	0.3	95-100	2.6
Penta	62.8-63.7	64.5	11	IV	0.5	105-120	2.5
		62.8	13	VI	0.3	100-109	4.7
		64.6	14	IV	0.2	105-123	5.2
Hexa	67.2-68.1	66.7	11	V	0.3	124-129	8.0
		66.4	11	VI	0.3	131-136	5.6
		68.9	11	VIII	0.4	141	0.8
		66.3	13	VIII	0.3	109-112	5.6
		67.0	13	VIIII	0.3	112-116	8.9
		67.8	13	IX	0.3	116-126	2.8
		68.5	13	X	0.3	126-132	4.5
		66.3	14	V	0.2	116-122	6.3
		67.2	14	VI	0.2	124-134	8.0
		68.4	14	VII	0.3	131-151	6.0

hexa-chloro addition product but this was not established.

These analytical data obtained from the reaction of ethyl benzene (II) with chlorine are in good agreement with the kinetic data.

III. Radiation Yields

Radiation yields have been calculated for the chlorination of ethyl benzene (II). These radiation yields have been expressed in terms of G values (molecules reacted per 100 electron volts of radiation energy absorbed) based on chlorine and are shown in Table IX. It is noted that separate G values have been given for the substitution and addition reactions.

The G values presented in Table IX have a possible deviation of ±5 percent. This possible deviation arises from assumptions made in the calculations. As in the case of naphthalene (5), the G values have been calculated for specific time intervals throughout the experimental runs.

The overall G value for 70 minutes for the substitution reaction at -25°C was some 30 percent greater than that at -5°C. Such a direct comparison of G values could be made for the addition reaction. The kinetic data indicated that the addition reaction at -25°C had barely reached its maximum reaction rate after 70 minutes. At -5°C the maximum addition reaction rate was reached much earlier. To obtain a valid comparison of G values for addition the reaction time would have to be increased to a point where the addition reaction had gone almost to completion. It may be of interest to note that, at the maximum

TABLE IX. G Values Based on Chlorine for the
Chlorination of Ethyl Benzene (II).

Reaction Temp. °C	Type of Reaction	G Values Based on Chlorine Time Intervals, minutes								Overall for 70 Minutes
		0-10	10-20	20-30	30-40	40-50	50-60	60-70	
-5	Substitution	81,600	81,600	81,600	81,600	81,200	80,600	70,900	79,900
-25	Substitution	142,000	142,000	139,000	137,000	93,300	46,200	30,200	104,000
-5	Addition	18,900	76,800	115,000	135,000	144,000	147,000	147,000	112,000
-25	Addition	1,970	6,900	23,600	72,600	136,000	183,000	210,000	90,600

addition reaction rates, the G value at -25°C is about 43 percent greater than that at -5°C.

DISCUSSION AND CONCLUSIONS

This study has demonstrated that ethyl benzene can successfully be chlorinated in the presence of gamma radiation. However, the study shows that the presence of impurities in the ethyl benzene can inhibit the reaction almost completely. These impurities are of a type which can be removed by treatment with sodium.

The presence of possible inhibitors in ethyl benzene (I) was suggested by the anomalous kinetic and analytical data that were obtained from the early experimental runs. In particular, the kinetic data for ethyl benzene (I) at -25°C showed a lower rate of addition in the irradiated run than in the non irradiated runs. Examination of the analytical data showed further discrepancies in the results. Further, the shape of the addition curves at -25°C did not conform to that generally expected on the basis of previous experience with the chlorination of other aromatic compounds.

It was subsequently established that ethyl benzene (I) was not a pure reagent. Treatment of ethyl benzene (I) with metallic sodium resulted in the removal of at least two foreign materials. The ethyl benzene (II) thus obtained exhibited a much different behavior during reaction than did ethyl benzene (I). The difference in reaction was assumed to result from some inhibiting effect of the foreign materials. At this writing

the impurities which were found in ethyl benzene (I) have not been identified.

Although the ethyl benzene (I) was dried and distilled prior to reaction, this general procedure was not effective in obtaining a reactant which was pure enough to allow reaction with chlorine. The ethyl benzene (I) used in part of the present study was the same reactant that was used in previous work reported from this laboratory. However, the earlier data and G values (3,4) are not in agreement with the present data, and this can be explained on the basis of the erratic reaction of an impure compound and a difference in the method of calculating G values. Several of the factors which are involved in the calculation of the earlier G values are listed in a report on the chlorination of mesitylene and naphthalene (5).

Pure ethyl benzene [ethyl benzene (II)] was found to react vigorously with chlorine in the presence of gamma radiation. Virtually no reaction was obtained without radiation. Thus, the reaction of chlorine with pure ethyl benzene was found to proceed only under the influence of gamma radiation. The analytical data obtained from product analyses supported the conclusions drawn from the kinetic data.

Since some chlorinated products were obtained with ethyl benzene (I) which were different in color from those obtained with ethyl benzene (II), it is possible that a reaction of chlorine with the foreign materials present in the former had occurred. In this case it might be that long continued chlorination of ethyl benzene (I) could result in removal of the foreign

materials by reaction. A reaction such as that obtained for ethyl benzene (II) could start if the concentration of the foreign materials in ethyl benzene (I) had decreased sufficiently.

Radiation yields for the reaction of chlorine with ethyl benzene (II) have been expressed in terms of "G" values (molecules reacted per 100 electron volts of radiation energy absorbed) in order to provide a comparison with other reactions found in the field of radiation chemistry. A discussion of several factors which are important in the interpretation of G values has been presented in an earlier report (5). The current G values have been based on chlorine.

SUMMARY

1. This study has presented data which illustrate the effect of impurities on the reaction of ethyl benzene and chlorine in the presence of gamma radiation.

2. The rates of chlorination of pure ethyl benzene have been measured under irradiated and non irradiated conditions.

3. The reaction of chlorine with pure ethyl benzene was found to proceed only in the presence of gamma radiation.

4. Kinetic data showed that ethyl benzene reacted with chlorine both by substitution and by addition.

5. Both the substitution and addition reactions were favored by low temperature. This observation indicates that the reaction rate is a function of the chlorine concentration in the reaction mixture.

6. Analytical data have indicated that the mono- and hexa-chloro derivatives of ethyl benzene are the primary products of reaction in the presence of radiation.

7. Radiation yields expressed as G values based on chlorine have been calculated for the chlorination of ethyl benzene. Maximum average G values of 104,000 for substitution and 112,000 for addition were obtained in a 70 minute reaction time.

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