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SULFOCHLORINATION OF HYDROCARBONS
INDUCED BY GAMMA RADIATION

by

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ABSTRACT

The purpose of this study was to determine the effect of gamma radiation on the direct sulfochlorination of hydrocarbons and nitrobenzene.

The radiation source consisted of spent uranium fuel elements, providing a gamma radiation intensity up to 2.5×10^6 roentgen/hour. The sulfochlorination studies were carried out either with SO_2Cl_2 or with gaseous mixtures of SO_2 and Cl_2 . Attempts to sulfochlorinate nitrobenzene and benzene were unsuccessful. There was no detectable reaction in the case of nitrobenzene, while the reaction with benzene produced only chlorinated products, up to the full addition product 1,2,3,4,5,6-hexachlorocyclohexane.

Liquid cyclohexane reacted with SO_2 and Cl_2 in the presence of gamma radiation to give very high yields of cyclohexanesulfonyl chloride, and to a smaller extent chlorocyclohexane and cyclohexanedisulfonyl chloride. The length of the chemical chain reaction induced by gamma radiation was estimated at over 2×10^5 , and the radiochemical yield G was greater than 10^6 . Sulfochlorination was the predominant reaction, but at lower radiation intensities and for SO_2/Cl_2 ratios lower than unity, chlorination was found to exceed sulfochlorination. Within a temperature range of 11.5 to 40.0°C , the selectivity of the reaction was independent of temperature. For a total gas flow rate of 1.9 l/min per liter C_6H_{12} and SO_2/Cl_2 ratios of 2/1, the rate of conversion to $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ was proportional to the square root of the absorbed radiation dose up to a dose rate of 40 rad/min, but became independent of dose rate above 400 rad/min. Under these conditions, the conversion rate was 0.025 g-moles $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}/(1) (\text{min})$. A basic plant design was developed for

the continuous sulfochlorination of cyclohexane initiated by gamma radiation. The economics of this process may become attractive with the expected availability of cheap radiation sources.

Solutions of cyclohexane, chlorine and sulfur dioxide in carbon tetrachloride were irradiated in an oxygen-free system. Reaction rates, equivalent to the rate of disappearance of free chlorine, were determined spectrophotometrically at $4000 \text{ \AA}$. The reaction products were cyclohexane-sulfonyl chloride and hydrochloric acid in nearly stoichiometric quantities. An empirical rate equation was derived, in which the rate of disappearance of chlorine was shown to be proportional to the square root of the product of absorbed radiation, chlorine and cyclohexane concentrations, and independent of the concentration of sulfur dioxide. A chain mechanism was proposed, and the rate equation derived from this scheme was found to be in excellent agreement with the empirical rate equation. The reaction proceeded by a free radical mechanism, as evidenced by the strong inhibiting effect of oxygen. G-numbers were of the order of 10^5 , corresponding to an estimated chain length of 5000, which is of the same order as the quantum yield of the photochemical sulfochlorination. Activation energies for the individual reactions were derived from the reaction rate constants at two temperatures and compared favorably with values reported for similar photochemical reactions.

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1. Introduction

The rapidly growing number of nuclear reactors during the years following World War II has greatly increased the supply of radioactive materials. While, in some cases, useful radioactive isotopes have been made from stable, naturally occurring elements (e.g., Co⁶⁰), the bulk of our present inventory of radioactive materials is represented by the elements created during the fission of uranium. These fission products are causing a serious problem: their intense radioactivity is damaging to the structural materials of the nuclear reactor and their absorption of neutrons interferes with the maintenance of a self-sustaining nuclear chain reaction. The equipment for the separation, storage and ultimate disposal of these unavoidable by-products of nuclear energy represents a large investment. This unfavorable economic factor, combined with the rising energy-consciousness of our generation, has stimulated considerable interest in the utilization of fission products for industrial applications.

The strong ionizing properties of nuclear radiation, particularly the penetrating gamma rays, suggested their application in the initiation of chemical reactions.

Though studies in radiation chemistry, which concerns itself with chemical changes occurring during the interaction of ionizing radiation with matter, date back as far as the turn of the century, these investigations were largely fundamental in character, without any practical consequences. Collinson and Swallow have published an extensive review of the radiation chemistry of organic substances.⁽¹⁶⁾ During the past 5 years, several investigations were reported which were directed towards the application of radiation to the chemical process industry.^(38,55)

Almost all previous studies in this field used some artificial isotope (generally Co^{60}) as the radiation source. In the present investigation, the gamma radiation actually originated from spent uranium fuel elements containing the fission products. This created some special problems with regard to the experimental equipment and the evaluation of absorbed energies.

The high yields obtained for the sulfochlorination of cyclohexane and the excellent selectivity of this chemical chain reaction would appear to make this or closely related processes promoted by gamma radiation of imminent interest to the process industry.

It is hoped that the results presented here will be helpful in the development of industrial applications for nuclear radiation, and that the derived kinetics of the reaction may be of some use in the design of chemical reactors.

2. Radiation Chemistry

In its wider meaning, radiation chemistry embraces the study of chemical effects produced by all types of radiation, and as such could have been considered an extension of photochemistry. In practice, however, radiation chemistry has been restricted to the study of the interaction with matter and subsequent chemical changes of several clearly defined types of ionizing radiation, notably alpha and beta particles, gamma and X rays, and, more recently, accelerated neutrons and protons.

Historically, the first "experiments in radiation chemistry" occurred simultaneously with the discoveries of the darkening of the photographic plate by X rays (Roentgen, 1895) and by radiations from uranium (Becquerel, 1890).

In the years following these discoveries many studies were conducted, notably by S. C. Lind and associates, on the effect of radiations on various chemical systems. During this early period, it was generally accepted that ionization was the exclusive mode of reaction,⁽⁵²⁾ making it customary to report results in terms of ion-pair yields, and the "cluster" theory enjoyed general acceptance. E. W. R. Steacie⁽⁷⁷⁾ believes that this preoccupation with ionization delayed until recently the recognition of the importance of excited molecules and of secondary reactions involving atoms and radicals.

The fundamental modern concept of radiation chemistry, that ions formed during the primary process do not react chemically in this state, but are first converted into excited molecules or atoms, was first advanced in 1936 by Eyring, Hirschfelder, and Taylor.^(20,21)

The interest of chemical engineers in the practical potentialities of radiation chemistry dates back only several years. It stems partly from the desire of tapping a huge reservoir of unused energy to promote reactions hitherto occurring only at extreme conditions of temperature and pressure, and partly from the expectation of uncovering new chemical processes in a way somewhat comparable to the revolutionary developments of applied catalysis.

2.1. Physical Phenomena

The interaction of gamma radiation with matter is a conversion of energy with a large change in entropy, because of the energy degradation which takes place. The primary events which occur during the energy-conversion phase are believed to proceed by three distinct processes in the range of photon energies of interest in radiation chemistry (about 0.10 to 5 Mev):⁽¹⁸⁾

(a) The photoelectric effect, in which all the energy of the photon is transferred to a bound electron. Part of this energy is used to overcome the binding of the electron to the atom and the rest is converted into kinetic energy. This effect predominates at low photon energies.

(b) The Compton effect (also known as scattering or Klein-Nishina effects) occurs when a photon strikes an atomic electron and is deflected from its original path. Over 99% of the gamma energy absorbed by the systems studied in this investigation was by Compton scattering.

(c) Pair production consists of the absorption of a gamma photon in the field of an atomic nucleus, with the production of an electron-positron pair. This effect becomes noticeable at energies higher than 1 Mev for elements with atomic numbers greater than 50.

The first consequence of the passage of a gamma photon through matter is the production of a large number of ions in its path, largely by the slowing down of the Compton electrons.

2.2. Chemical Phenomena

During the first three decades of radiation chemistry, it was generally believed that the ions formed by the interaction of radiation with matter participated directly in the subsequent chemical reactions. The mechanism was explained by Lind as the formation of "clusters," consisting of a number (specific for the particular system) of neutral molecules, grouped around an original ion and sharing its charge.⁽⁵²⁾ The final chemical product was formed by neutralization of this cluster by an electron or negative ion. It is now believed⁽⁷⁷⁾ that the primary process leads both to ionization and to the formation of excited molecules. The primary ions are then neutralized⁽³⁹⁾ by thermal electrons to give additional excited molecules. These excited molecules may either dissipate their energy by collision with other molecules, without the formation of a new chemical product, or they may decompose into free radicals and atoms which subsequently undergo reactions generally associated with such species. These probable steps are summarized in the following table:

This mechanism accounts for the generation of free radicals which are necessary for the initiation of chemical chain reactions, such as the

sulfochlorination of cyclohexane which was studied in detail in the present investigation.

The actual existence of free radicals in irradiated systems has been demonstrated by various methods: interception (scavenging) with reactive substances, e.g., triphenylmethane,⁽⁶⁹⁾ diphenylpicrylhydrazyl⁽⁹⁾ and others (Schuler has recently reviewed various methods for the detection of free radicals in hydrocarbon radiolysis by scavenger methods);⁽⁷⁰⁾ initiation of chain reactions, known to proceed only by a free radical mechanism, e.g., the polymerization of vinyl monomers;⁽⁹⁾ examination of the hyperfine structure of the absorption bands obtained by electron paramagnetic resonance spectroscopy.⁽⁸⁵⁾

3. Sulfochlorination of Organic Compounds

The introduction of the $\text{-SO}_2\text{Cl}$ group into an organic molecule by a large variety of methods is designated as sulfochlorination.

The resulting sulfonyl chlorides are quite reactive, which makes them valuable intermediates in organic synthesis. Numerous applications have been cited for sulfonyl chlorides, ranging from the use of a derivative of methanesulfonyl chloride in the treatment of leukemia⁽³¹⁾ to the recently introduced synthetic rubber "Hypalon," which is a modified polyethylene containing -Cl and $\text{-SO}_2\text{Cl}$ groups.⁽⁸⁴⁾ Extensive reviews of the chemistry of sulfonyl chlorides have been published,^(19,57,61) and annual reviews of the literature appear as part of the "Unit Processes Review" in Industrial and Engineering Chemistry.

The reviews cited^(19,57,61) contain a summary of all types of syntheses for aliphatic and aromatic sulfonyl chlorides published up to 1954.

Following are some of the conventional methods for the preparation of aliphatic sulfonyl chlorides:

Reaction of dry aliphatic sulfonic acids or sulfonic acid salts with PCl_5 or POCl_3 .^(59,64,73) Sulfuryl chloride can be used to introduce the $\text{-SO}_2\text{Cl}$ group into an aliphatic hydrocarbon with the aid of catalysts such as dibenzoylperoxide,⁽⁷²⁾ aluminum chloride,⁽⁴⁸⁾ light and pyridine.⁽⁴⁷⁾ Reaction of aliphatic mercaptanes, sulfides, disulfides and xanthates with chlorine,^(22,44,78,82,87) chlorination of alkylthiocyanates and alkylthiosulfates.^(43,88)

Of particular interest have been methods for the direct sulfochlorination, using simple reactants such as hydrocarbons, $\text{SO}_2 + \text{Cl}_2$, and SO_2Cl_2 . The Reed reaction for aliphatic hydrocarbons,⁽⁶⁵⁾ which has

attracted considerable attention from the chemical industry, proceeds in the presence of actinic light as follows:

A chain mechanism for this reaction has been proposed by Kharasch⁽⁴⁶⁾ and was verified experimentally by Stauff.⁽⁷⁶⁾

Several claims were made in the patent literature to the effect that this method proceeds not only with aliphatic and cycloaliphatic hydrocarbons, but also with aromatic hydrocarbons,⁽⁶⁶⁾ alkylated aromatic hydrocarbons,⁽²⁷⁾ olefins,⁽⁶⁷⁾ alcohols,⁽²⁸⁾ etc. However, it was definitely established that the Reed reaction does not proceed with aromatic hydrocarbons, but only with saturated hydrocarbons or such derivatives which contain, in addition to a functional group, one or more methylene groups.⁽¹⁹⁾ Depending on the particular reaction conditions, chlorination takes place in addition to sulfochlorination. The general features of the photochemical sulfochlorination of hydrocarbons were summarized by Kroepelin.⁽⁴⁹⁾ The ratio of chlorination to sulfochlorination decreases with an increase in light intensity (up to an "optimal value"), with shorter wavelengths, with an increase of the SO_2/Cl_2 ratio in the feed gas (up to a ratio of 1.3/1), with a decrease in temperature, and with a reduction in bubble size. Certain catalysts, capable of generating free radicals, can be substituted for light, e.g., peroxides,⁽³⁰⁾ tetraethyl lead,⁽²⁹⁾ etc.

Gaseous hydrocarbons are best sulfochlorinated by dissolving them in an inert solvent (usually CCl_4); with liquid hydrocarbons, the Cl_2/SO_2 feed gas is bubbled through the illuminated liquid; solid hydrocarbons are either molten or suspended as fine particles in CCl_4 .⁽⁵⁶⁾ At high conversions, disulfonyl chlorides are also formed. Asinger has shown⁽³⁾

that the substitution rule by Hass⁽³⁵⁾ applies equally well to sulfochlorination (i.e., secondary hydrogen atoms are substituted 3.25 times faster than primary hydrogen atoms).

Aromatic sulfonyl chlorides cannot be prepared by initiation with free radicals. A summary of all published methods of preparation was presented by Muth.⁽⁵⁷⁾ The most common procedures start with aromatic sulfonic acids or sulfonic acid salts which are reacted with various chlorinating agents, such as PCl_5 , POCl_3 , $\text{PCl}_3 + \text{Cl}_2$, $\text{C}_6\text{H}_5\text{CCl}_3$, COCl_2 , and ClSO_3H . Among the more direct sulfochlorinating methods for aromatic hydrocarbons are: Reaction with chlorosulfonic acid (technically probably the most important method) and reaction with SO_2Cl_2 and AlCl_3 (Friedel-Crafts).⁽¹²⁾ Another important method consists of chlorinating aromatic disulfides, preferably in the presence of other oxidizing media, in accordance with the following reaction:⁽⁶²⁾

The possible utilization of gamma radiation for the promotion of chemical chain reactions in general, and sulfochlorination in particular, was suggested in 1953 at a symposium on fission products at Harwell, England.⁽¹⁾ However, only one paper,⁽³⁷⁾ on the sulfochlorination of heptane with gamma rays from Co^{60} , has appeared, so far, in the literature.

4. Equipment

4.1. Gamma-Irradiation Facility

All irradiations were performed in the Argonne High-Level Gamma-Irradiation Facility (Figure 1). The radiation source consisted of spent fuel elements from the Idaho Materials Testing Reactor, containing a large number of highly radioactive elements from the fission of enriched uranium. The box-like fuel elements are made up of a number of concave-shaped plates composed of a uranium-aluminum core clad with aluminum. A gamma flux of up to 2.5×10^6 roentgens/hour is obtainable with fresh fuel elements, but for the present work irradiations were carried out with aged fuel elements, providing a flux up to 400,000 r/hr. Lower gamma intensities were obtained by placing the reactor at varying distances from the radiation source.

The irradiation rack, containing the radioactive fuel elements, is located on the floor of a canal filled with 55,000 gallons of water; this provides an effective shielding of 20 feet of water. The shielding water is continuously circulated through a mixed-bed ion exchange column, to maintain a minimum resistivity of 200,000 ohm-cm and a pH of 7. This is necessary to avoid corrosion of the fuel elements and also to remove small amounts of radioactivity introduced into the water from the fuel-element cladding. The glass reactors used in this study were contained in thin-walled (1/16 in.) aluminum sample urns, 4-1/8 in. in diameter by 28 in. in height and weighted at the bottom to overcome buoyancy. A special urn cover (Figure 2), provided with a water-tight cable connector, was fabricated. A heavy-duty rubber cable, containing all supply and withdrawal lines as well as thermocouple and electrical wires, was connected to the urn cover. The loaded urn was lowered into the rack and raised to

FIGURE 1. ARGONNE HIGH LEVEL GAMMA IRRADIATION FACILITY

FIGURE 2. IRRADIATION URN COVER WITH CABLE CONNECTOR

the operating level with an overhead electric hoist. Figure 3 shows the position of the urn during irradiation.

4.2. Chemical Reactors and Accessories

Irradiations were carried out in two types of reactors: a liquid-phase reactor for the experiments with SO_2Cl_2 , and a gas-liquid reactor for the runs with gaseous SO_2 and Cl_2 mixtures. Water circulating through the jackets of either reactor permitted control of the temperature inside the reactor to within 0.2°C . The circulating water was pumped through a reservoir, equipped with a Freon compression refrigerator, electric heater, temperature controller and electric stirrer.

The liquid-phase reactor consisted of a 100-ml round bottom flask, mounted inside a gasketed glass vessel, through which the temperature-controlling fluid was circulated. A glass thermocouple well, extending into the center of the reactor, contained a copper-constantan thermocouple which was connected to a "Brown" temperature recorder-controller. Off-gases were vented through a side-arm which was connected through $1/4$ in. polyethylene tubing and a CaCl_2 drying tube to an external vent. Excellent agitation of the liquid inside the reactor was obtained with a magnetic stirring bar, actuated by a variable speed motor located underneath the reactor.

The gas-liquid reactor (Figure 4) consisted of two concentric Pyrex tubes, the dimensions of the inner tube being $7/16$ in. I.D. and its length 22 in., with water circulating in the outer annulus at a rate of 800 cc/min. The reactor was provided at the bottom with a fritted-glass inlet for gases and at the top with a standard taper, ground-glass closure through which the thermocouple well protruded to the center of the reactor. Off-gases were vented through a glass side-arm. In the kinetics runs, the reactor top consisted of a spherical reservoir with a two-way stop-cock for the withdrawal of samples and the venting of gases, respectively.

FIGURE 3. VIEW OF IRRADIATION FACILITY, SHOWING URN AND CABLE DURING IRRADIATION

FIGURE 4. GAS-LIQUID REACTOR, ALUMINUM
STAND AND SUPPLY LINES

The reactor was mounted with stainless steel springs on an aluminum frame which fitted snugly into the aluminum irradiation urn, to ensure good duplicability in positioning the reactor relative to the fuel elements. The gas-dispensing system (Figures 5, 6 and 7) consisted of cylinders of liquid Cl_2 and SO_2 (at least 99.5% pure), two carefully calibrated metering cylinders, and pressure gauges. The exact amount of gas contained in the metering cylinder was obtained from the respective pressure readings and the ambient temperature. During the kinetics experiment, when the amounts of gas delivered to the reactor were much smaller, calibrated sections of 1/4 in. copper tubing were used instead of the metering cylinders.

Initially, one cylinder was used to blend the SO_2/Cl_2 mixture to the desired compositions, but because of the formation of SO_2Cl_2 in the blending cylinder (at room temperature the equilibrium favors the formation of SO_2Cl_2 , the dissociation constant being only 0.0288 at 30°C) a large error resulted in the metering of the gas mixture. When two metering cylinders were used, the extent of SO_2Cl_2 formation in the supply lines was found to be negligible. An inert gas cylinder (nitrogen for the process study and argon for the kinetics phase) was also connected to the gas manifold for the purging of the system before and after a run. In the kinetics studies, argon was also used to convey small amounts of Cl_2 and SO_2 into the glass reactor.

The approximate flow rate of gas was estimated by means of gas bubblers filled with concentrated H_2SO_4 . The exact flow rate was obtained from frequent pressure readings for the gas contained in the metering cylinders. Exit gases, consisting of unreacted Cl_2 and SO_2 , and also some SO_2Cl_2 and HCl , were bubbled through 10% NaOH before being vented outside the building. Copper tubing (1/4 in.) and brass fittings were

FIGURE 5. EQUIPMENT FOR SULFOCHLORINATION STUDIES

FIGURE 6. GAS METERING AND DISPENSING SYSTEM

FIGURE 7. GAS ABSORPTION TRAIN AND BECKMAN SPECTROPHOTOMETER

used for the high-pressure section, while glass, rubber and polyethylene tubing were used for the low-pressure section. Figure 8 is a schematic diagram of the apparatus.

Before use, the entire system was carefully checked for leaks in the following manner:

(a) The system was pressurized with N_2 to about 10 psig and any pressure decrease was noted for a period of 5 hours. This helped to locate and eliminate all relatively large leaks.

(b) The system was filled with N_2 and a small amount of SO_2 . Small leaks were easily located by the fog formation, when an open flask with NH_4OH was held in the proximity of the leak.

(c) Very small leaks were finally located with a General Electric Halogen detector.

The gas metering system was mounted on a mobile bench which was enclosed in a heavy-gauge polyethylene tent provided with an electric blower exhausting to the outside of the building. Manometers filled with Hg (protected by small amounts of CCl_4 from the attack by Cl_2) were located on either side of the reactor, to determine pressure drops and to serve as pressure relief in case of unexpected pressure build-up (plug-up in the reactor or gas supply lines). The inlet side manometer was equipped with an electrical alarm, actuated if the pressure exceeded a pre-set value. The entire system could also be evacuated to a pressure below 1 mm Hg with a mechanical vacuum pump, protected by a KOH-silica gel absorption column and a low temperature trap.

A low-pressure distillation still with an 18 in. entrainment separating column was used for the removal of volatile constituents in the reaction products.

FIGURE 8. APPARATUS FOR SULFOCHLORINATION STUDIES

4.3. Materials

The following materials were used during the radiochemical syntheses:

<u>Material</u>	<u>Grade</u>	<u>Supplier</u>	
SO ₂ Cl ₂	Practical	Eastman	B.P. 69.5°C
C ₆ H ₅ NO ₂	White-Label	"	M.P. 5-6°C
C ₆ H ₆	ACS Anal. Reag.	Mallinckrodt	B.P. 80.1 (± 0.25)°C Thiophene free
CCl ₄	Spectro	Eastman	B.P. 76.1 - 76.3°C
C ₆ H ₁₂	White-Label*	"	M.P. 4 - 5.5°C
C ₆ H ₁₂	Spectro**	"	M.P. 4 - 5.5°C
Cl ₂		Matheson	Min. Purity: 99.85%
SO ₂		Ohio	Min. Purity: 99.5%

* For process study

** For kinetics study

5. Analytical Methods

5.1. Chemical Methods

5.1.1. Determination of Hydrolyzable Chlorine

The chlorine introduced during sulfochlorination is directly attached to the sulfur, as part of the $\text{-SO}_2\text{Cl}$ group. Depending on the experimental conditions, chlorination takes place to varying degrees, but in this case the chlorine is attached to the carbon atoms. In the former case the chlorine is hydrolyzable and can be determined by acid-base titration. The method finally adopted was a nonaqueous titration with 0.1 N NaOCH_3 in a $\text{C}_6\text{H}_6:\text{CH}_3\text{OH} = 6:1$ medium, using thymol blue as an indicator. The sodium methylate solution was standardized with primary standard grade benzoic acid.

The following results are an indication of the accuracy and precision obtainable with this method.

<u>Material</u>	<u>Source</u>	<u>Hydrolyzable Cl, %</u>	
		<u>Found</u>	<u>Calculated</u>
$\text{p-NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	E-K	15.9	16.0
m- "	E-K	15.9	16.0
$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$	E-K	19.8	20.1
$\text{C}_6\text{H}_5\text{Cl}$	E-K	0.0	0.0
C_6Cl_6	E-K	0.0	0.0
$\text{C}_6\text{H}_6\text{Cl}_6$	E-K	0.0	0.0
50% $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ } 50% C_6Cl_6 }	E-K	10.1	10.1
50% $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ } 50% $\text{C}_6\text{H}_5\text{Cl}$ }	E-K	10.3	10.1

<u>Material</u>	<u>Source</u>	<u>Hydrolyzable Cl, %</u>	
		<u>Found</u>	<u>Calculated</u>
50% C ₆ H ₅ SO ₂ Cl } 50% C ₆ H ₆ Cl ₆ }	E-K	10.1	10.1
C ₆ H ₁₁ SO ₂ Cl	A.S.	19.2	19.4

For ten replicates for p-NO₂C₆H₄SO₂Cl (approximate sample weight - 0.250 g) the average was 15.87 and the standard deviation ± 0.134 or $\pm 0.8\%$.

5.1.2. Determination of Total Sulfur

The classical Carius combustion method was used. The sample, weighing about 0.020 g, NaCl (about 100% equivalent excess) and 0.5 ml HNO₃ (fuming) were sealed in a special heavy-wall glass tube and heated for 5 hours at $255 \pm 10^\circ\text{C}$. The resulting Na₂SO₄ was titrated with 0.02 N BaCl₂ (standardized with K₂SO₄) using disodium tetrahydroquinone (THQ) as an indicator. The titration was carried out in a 50% ethanol medium and at a pH of 7.0. A small amount of AgNO₃ was added to form an AgCl precipitate, which made the end-point perception much easier.

This method was quite time-consuming and, after the equivalency of S with hydrolyzable Cl had been established during initial runs, the determination of S was discontinued. Following are some of the results obtained:

<u>Material</u>	<u>Source</u>	<u>Sulfur %</u>	
		<u>Found</u>	<u>Calculated</u>
p-NO ₂ C ₆ H ₄ SO ₂ Cl	E-K	14.2	14.4
C ₆ H ₆ Cl ₆	A.S.	0.0	0.0
C ₆ H ₁₁ SO ₂ Cl	A.S.	17.3	17.5

For five replications with p-NO₂C₆H₄SO₂Cl:

Average: 14.20%; St. Dev.: ± 0.123 or $\pm 0.8\%$

5.1.3. Determination of Total Chlorine

The method of Liggett⁽⁵¹⁾ was adopted. A reagent was first prepared by reacting finely dispersed metallic sodium with biphenyl in a toluene and ethylene glycol dimethyl ether medium. This reagent was then reacted with the sample (about 0.250 g) dissolved in toluene, and the resulting NaCl was extracted with water and 3 N HNO₃. The chloride was at first determined by the Volhard method, but it was found that C₆H₁₁SO₂Cl and C₆H₁₁Cl synthesized with gamma radiation gave an aqueous extract which produced a red coloration with ferric alum, the indicator for the Volhard method. Gravimetric determination of the AgCl was used instead throughout the process study of the sulfochlorination of cyclohexane. It was also noticed that compounds containing an NO₂ group gave dark extracts, making impossible subsequent chloride determinations by the method of Volhard. This interference was overcome by purification with activated carbon and vacuum filtration prior to the titration. Following are some of the results obtained:

<u>Material</u>	<u>Source</u>	<u>Total Chlorine, %</u>	
		<u>Found</u>	<u>Calc.</u>
C ₆ Cl ₆	E-K	74.3	74.8
C ₆ H ₅ SO ₂ Cl	E-K	20.3	20.1
p-NO ₂ C ₆ H ₄ SO ₂ Cl	E-K	15.7	16.0
C ₆ H ₆ Cl ₆	E-K	73.1	73.2
C ₆ H ₆ Cl ₆	A.S.	73.0	73.2

For five replications with C₆H₆Cl₆:

Average: 73.08; St. Dev.: ± 0.087 or ± 0.12%

5.1.4. Determination of the Sulfonyl Chloride Group

A specific method for the determination of the sulfonyl chloride group was very desirable, particularly as a qualitative test during the exploratory phase of this study.

It was found that both aliphatic and aromatic amines react in the presence of pyridine to give deeply colored sulfonamide complexes. Diluted solutions of these complexes were found to obey the Beer-Lambert absorption law, suggesting a possible adaptation for quantitative determinations. It appeared, however, that the presence of some compounds which alone gave no color reaction affected the color intensity produced by the sulfonyl chloride group. Nevertheless, this test was very useful for qualitative determinations, permitting the detection of as little as 2×10^{-5} g of a sulfonyl chloride compound per liter. The specificity of this test can be seen from the following table:

Compound	Color Reaction with		
	Aniline	p-Toluidine	2-Aminofluorene
$C_6H_5SO_2Cl$	O-R	R.	N.D.
m- $NO_2C_6H_4SO_2Cl$	O-R	O-R	R.
p- $NO_2C_6H_4SO_2Cl$	O-R	O-R	R.
C_6H_5Cl	N.D.	none	N.D.
O- $NO_2C_6H_4Cl$	N.D.	Y.	N.D.
m- "	N.D.	D.Y.	N.D.
p- "	N.D.	P.Y.	N.D.
$C_6H_5NO_2$	Y.	Y.	N.D.
C_6H_6	none	none	N.D.
C_6Cl_6	none	none	N.D.
$C_6H_6Cl_6$	none	none	N.D.

Compound	Color Reaction with		
	Aniline	p-Toluidine	2-Aminofluorene
SO ₂ Cl ₂	D.B.	D.B.	N.D.
p-CH ₃ C ₆ H ₄ SO ₂ Cl	N.D.	R.	N.D.
C ₆ H ₁₁ SO ₂ Cl	N.D.	R.	N.D.

Code: D.B. - dark brown; D.Y. - deep yellow;

N.D. - not determined; O. - orange;

P.Y. - pale yellow; R. - red; Y - yellow.

5.1.5. Gas Analyses

In the course of this study it was frequently desirable to determine chemically the composition of Cl₂ and SO₂ gas mixtures.

A satisfactory method, which consisted of absorbing the gas mixture in an aqueous solution containing 2.5% NH₃ and 1.0% H₂O₂, was worked out. The solution was then boiled to expel all unreacted NH₃, decompose H₂O₂, and quantitatively convert any NH₄OCl present into NH₄Cl. After boiling, the solution was neutralized with either NaOH or HNO₃ to a pH of 6.8 to 7.2. Traces of H₂O₂ which interfered with the sulfate determination using a THQ indicator were completely decomposed with a drop of catalase enzyme. Cl⁻ was then determined by Volhard titration and SO₄²⁻ by titration with BaCl₂. Typical results are shown below:

Cl₂ -- Taken: 250 ml at 24°C and 734 mm Hg:

$$\text{Calculated: } \frac{0.250}{22.4} \times 71.0 \times \frac{734}{760} \times \frac{273}{297} = 0.704 \text{ g Cl}_2$$

Found: 0.710 g Cl₂

SO₂ -- Taken: 250 ml at 24°C and 734 mm Hg:

$$\text{Calculated: } \frac{0.250}{22.4} \times 64.1 \times \frac{734}{760} \times \frac{273}{297} = 0.633 \text{ g SO}_2$$

Found: 0.634 g SO₂

5.2. Spectrophotometric Methods

Infrared spectroscopy is widely used for the identification of functional groups. It was, therefore, assumed that the scanning of the infrared spectra may provide a guide in identifying the products synthesized during the exploratory phase of this study. A double-beam Perkin-Elmer Infrared Spectrometer was used with NaCl liquid cells. Unfortunately, very few spectra were available in the literature for the potential reaction products, which necessitated the compilation of a reference file. Eventually, the work was limited to distinguishing between $\text{-CSO}_2\text{Cl}$ and -CCl groups in the products synthesized with gamma radiation. Spectra were obtained for 1 and 5% solutions in CCl_4 and C_6H_{12} , compensated by an equal thickness of the respective solvent.

Sharp absorption bands were found for the $\text{-SO}_2\text{Cl}$ group at $1161 - 1165 \text{ cm}^{-1}$ and $1370 - 1376 \text{ cm}^{-1}$. This agrees very closely with the bands for $\text{-SO}_2\text{Cl}$ reported for "Hypalon"⁽⁷⁵⁾ and also for $\text{-SO}_2\text{Cl}$ in a recent compilation of infrared spectra.⁽⁶⁾ By this method it became possible to detect positively the presence of sulfonyl chlorides at concentrations above 1%. As a qualitative test, the infrared method had one advantage over the colorimetric test described in Section 5.1.4.: the possibility of distinguishing between SO_2Cl_2 and an organic sulfonyl chloride. Sulfuryl chloride, similar to organic sulfonyl chlorides, gave a brown-red coloration with the pyridine- p-toluidine reagent and also absorbed around 1162 cm^{-1} . However, the absorption band at 1370 cm^{-1} was absent in the infrared spectrum of SO_2Cl_2 . This difference is probably due to the fact that the absorption around 1370 cm^{-1} can be attributed to the C-SO₂-group⁽¹⁷⁾ which is obviously absent in SO_2Cl_2 . Infrared spectra

were helpful in the present work in definitely proving that sulfo-chlorination of aromatic compounds (C_6H_6 , $C_6H_5NO_2$) cannot be accomplished directly with gamma radiation.

It was originally intended to use infrared absorption measurements for quantitative determinations of $C_6H_{11}SO_2Cl$ during the kinetics studies of the sulfochlorination of C_6H_{12} . It appeared, however, to be much simpler to follow reaction rates by measuring the disappearance of Cl_2 , from absorption measurements at $4000 \text{ \AA}$, once the stoichiometric relation had been established.

During the exploratory work with the system $C_6H_6 - SO_2Cl_2$, it was found to be difficult to remove all of the SO_2Cl_2 from the reaction products. SO_2Cl_2 absorbs very strongly in the ultraviolet around $2800 \text{ \AA}$, and, by measuring the absorbance of the reaction products at this wave length, it was possible to detect as little as 0.001% SO_2Cl_2 .

Colorimetric measurements were carried out in an attempt to develop a quantitative method for the determination of organic sulfonyl chlorides, based on the color formation with a pyridine- p-toluidine reagent. This approach was abandoned when it appeared that the color intensity changed with time and was also affected by the presence of certain substances.

The rate of disappearance of Cl_2 was very conveniently measured with a Beckman Model B Spectrophotometer at $4000 \text{ \AA}$. At this wave length, Cl_2 was the only strongly absorbing substance in the system. A calibration curve (Figure 9) for the optical density of Cl_2 in CCl_4 at $4000 \text{ \AA}$ was obtained by extracting the CCl_4 solutions with 2.5% NH_3 , boiling the extract, and titrating with $AgNO_3$ to determine the Cl^- content, using a fluorescein indicator.

FIGURE 9. OPTICAL DENSITY - CONCENTRATION CURVE
FOR Cl_2 IN CCl_4

6. Radiation Dosimetry

6.1. Experimental Procedure

The gamma-radiation intensity was determined with a modified Fricke ferrous sulfate dosimeter,⁽⁷⁹⁾ which is based on the proportionality between the absorbed amount of gamma energy and the number of Fe^{++} atoms oxidized to Fe^{+++} . The dosimetry solution contained

0.001 N FeSO_4

0.8 N H_2SO_4

0.001 M NaCl .

The presently accepted G-value (number of atoms reacting per 100 ev of absorbed energy) for this reaction is 15.6 ± 0.3 .⁽⁴⁰⁾ The concentration of Fe^{+++} ions is measured directly, by determining the optical absorbance at a wave length of 3020 Å.

The dosimetry solution was contained in a duplicate reactor and the same geometrical relation prevailed as during an actual run. This was found to be more practical than the determination of the gamma intensity at several points, followed by mathematical integration over the entire reactor volume. After withdrawal from the irradiation site, the dosimetry solution was thoroughly mixed and sampled. The measured Fe^{+++} concentration thus reflected the average gamma dose received by the liquid in the reactor.

The logarithm of the experimentally determined dose rates were plotted against time, resulting in fairly straight lines. The slope changed slowly with time, because of the variations in relative composition of the fission products in the radiation source, caused by the depletion of short-lived radioisotopes.

6.2. Calculation of Absorbed Gamma Energies

The chemical dosimeter used in the present study for the estimation of the radiation intensity was only a measure of the gamma energy absorbed by the dosimetry solution. The experimentally determined values were converted to give the amount of gamma energy which would be absorbed by pure water exposed to an identical flux and for the same geometrical configuration. (79)

The organic solutions irradiated in this investigation have different absorption properties and, since radiochemical yields must be related to the actual quantity of absorbed energy, it was necessary to establish a relation between the absorbed energy and the radiation intensity obtained from the dosimeter.

The absorption equation for gamma radiation is (18)

$$B = B_0 \exp (-\mu x)$$

where

B_0 = number of photons in the incident beam

B = " " " remaining in the beam after
passing through the absorber

μ = absorption coefficient, cm^2/g

x = thickness of material traversed, g/cm^2 .

The number of absorbed photons, which is proportional to the absorbed energy, is given by the following relation:

$$B_{\text{abs}} = B_0 - B = B_0 - B_0 \exp (-\mu x) = B_0 [1 - \exp (-\mu x)] .$$

The term $\exp (-\mu x)$ can be expanded into the infinite series

$$1 - \frac{\mu x}{1!} + \frac{(\mu x)^2}{2!} - \frac{(\mu x)^3}{3!} + \dots \dots \dots \frac{(\mu x)^n}{n!}$$

All terms to a power higher than the first are small and can be disregarded. Substituting, one obtains the number of absorbed photons:

$$B_{abs} = B_0 \left(1 - 1 + \frac{\mu x}{1} \right) = B_0 \mu x$$

For identical gamma flux and geometry, the energies absorbed by two media, having negligible or comparable beam attenuation, are in the same ratio as their absorption coefficients. This relation is used to estimate the dosage received by the irradiated solution from the dosage measured with a chemical dosimeter, e.g., ferrous sulfate in 0.8 N H₂SO₄.

Thus (34)

$$E_s = E_D \frac{\mu_s}{\mu_D}$$

where

E_s = dosage in solution

E_D = " " dosimetry solution

μ_s = energy absorption coefficient (on a volume basis)
for solution

μ_D = energy absorption coefficient (on a volume basis)
for dosimeter.

For the range of photon energies from the source used in these irradiations and the type of atoms present in the irradiated materials, the gamma absorption takes place entirely by electron scattering (Compton effect), while the photoelectric and pair production effects are quite negligible, as will be shown later.

The absorption coefficient for Compton scattering is given (50)

by

$$\mu = \sigma_{kn} N_e$$

where

σ_{kn} = cross section for particular type of energy
(can be calculated from the Klein-Nishina
formula; the integrated function contains the
photon energy as the only independent variable)

N_e = number of electrons per unit volume.

Since σ_{kn} will be the same for the dosimeter and the irradiated solution, the previously derived expression for the dosage received by the irradiated solution becomes

$$E_S = E_D \frac{(N_e)_S}{(N_e)_D}.$$

This relation was used to calculate the amount of energy absorbed by the irradiated solutions.

Most of the gamma irradiations reported in the literature were done with Co^{60} or similar sources, which emit photons of particular energies. However, in the present study, the radiation source consisted of a large number of radioactive elements produced by the fission of uranium in a nuclear reactor. Since both the half-lives and the photon energies differ for each isotope, the energy distribution will also vary with time. An experimental determination of the energy spectrum would have been difficult, because of the location of the source under 20 ft of water.

A sufficiently close approximation can be made if the irradiation time in the nuclear reactor and the duration of the subsequent "cooling" period outside the reactor are known. Curves presenting the distribution of photon energies as a function of irradiation and cooling periods are given in reference (11).

The irradiation and cooling periods for the fuel rod used during the kinetics studies were 48 and 300 to 360 days, respectively. The gamma-energy distribution is as follows:

<u>Energy Range, Mev</u>	<u>Percent of Total Gamma Energy in Range</u>
0.20 - 0.25	11.1
0.25 - 0.32	-
0.32 - 0.40	-
0.40 - 0.50	-
0.50 - 0.63	2.2
0.63 - 0.79	5.3
0.79 - 1.00	74.8
1.00 - 1.26	<u>6.6</u>
Total	100.0

The irradiated solutions contained mainly three elements: H, C, and Cl. Absorption coefficients have been published for H and C⁽⁸⁶⁾ and were calculated for Cl by interpolation from the published values for S and A, which are on either side of Cl in the periodic table.

For the gamma-energy distribution shown above, the percent of the total energy absorbed by the above elements by Compton scattering is as follows:

H ----- 100%
 C ----- 100%
 Cl ----- 99.7%.

This fully justifies the assumptions made in the later calculations of the "Absorption Dose Factors," that the energy is absorbed exclusively by Compton scattering and can therefore be estimated from the electron densities of the elements present.

In the present study, the rad ("radiation absorbed dose") was used as the unit for the measurement of absorbed energy (1 rad = 100 erg of absorbed energy per gram). The rad is thus not a direct measure of the intensity of the gamma flux, since it depends on the absorption properties of the particular substance. If these properties are known in addition to the energy spectrum of the gamma radiation, it is possible to calculate the absolute intensity of the incident radiation in roentgen (r) units.⁽⁴²⁾ The "r" has been defined as the amount of radiation producing through ionization 1 electrostatic charge unit in 1.293 mg of air or, in energy equivalents, 87.7 erg/g of air.

7. Exploratory Reactions

The choice of a chemical system was rather difficult, because very few types of successful syntheses by gamma radiation have been reported in the literature. Criteria which guided in the selection of some of the systems were:

- (a) a relatively good radiochemical yield (high G-number);
- (b) present method of production requires extreme conditions of temperature or pressure, expensive catalyst and gives small yields;
- (c) relatively high cost of product;
- (d) reaction should proceed by a free radical mechanism, preferably as a chain reaction; and
- (e) product should be stable to radiolysis.

Direct sulfochlorination was selected because of numerous evidences in the literature that reactions of alkanes and cycloalkanes with mixtures of SO_2 and Cl_2 and also with SO_2Cl_2 are free radical-induced chain reactions.⁽⁸³⁾ Aromatic hydrocarbons were known to react predominantly with the Cl in the system, giving sulfonyl chlorides only in the presence of catalysts, e.g., AlCl_3 . The sulfonyl chlorides of nitrobenzene are very valuable starting materials in the synthesis of sulfa-drugs, and the failure of previous attempts to introduce an SO_2Cl group directly stimulated the exploration of the action of gamma radiation for this system.

7.1. The System Nitrobenzene + Sulfuryl Chloride

The sulfonyl chlorides of nitrobenzene are important intermediates in the dye and pharmaceutical industries, because of the large number of reactions made possible by the reactive sulfonyl chloride group. Thus,

for example, p-nitrobenzenesulfonyl chloride

is a very useful intermediate in the manufacture of sulfanilamide derivatives (sulfa drugs) which are sensitive to strong acids and alkalies, because the nitro group can be reduced to the amino group under nearly neutral conditions.⁽⁶⁰⁾ This is an advantage over p-acetylamino benzene-sulfonyl chloride, the intermediate most widely used for the preparation of sulfanilamide derivatives, since the troublesome hydrolysis of the acetyl group is avoided.

One possible method for the synthesis of p-nitrobenzenesulfonyl chloride, patented by Allied Chemical and Dye Co., is as follows:^(2,24)

The purification of the product thus prepared is quite difficult.

In selecting the system $C_6H_5NO_2 + SO_2Cl_2$ for exploratory irradiations, the assumption was made that sufficient nitrobenzyl free radicals would be produced by irradiation to start a chain reaction similar to that proposed by Kharash for the catalytic sulfochlorination of aliphatic hydrocarbons:⁽⁴⁵⁾

This assumption was further supported by the relatively high G-number of 4.5 reported for free radicals formed in $\text{C}_6\text{H}_5\text{NO}_2$ irradiated by gamma rays. (63)

Several experiments were carried out, using the reactor for liquids described in Section 4.2., at temperatures of 8, 25, and 50°C, total gamma doses of 0.47, 3.77 and 5.31 megarad, at an average radiation intensity of 4,300 rad/min, and a volumetric ratio of $\text{SO}_2\text{Cl}_2:\text{C}_6\text{H}_5\text{NO}_2$ of 8:5.

The color of the irradiated liquid turned dark red; however, this is not likely to be due to any chemical reaction, since the same color formation was noted when pure nitrobenzene was irradiated. The reaction products were subjected to fractional distillation at a pressure of 10-15 mm Hg. The nitrobenzene residue was analyzed for $-\text{SO}_2\text{Cl}$, S and Cl, all results being negative. The infrared spectrum did not differ from that of pure, unirradiated nitrobenzene.

The failure of nitrobenzene to react at all under irradiation could possibly be explained by the strong electropositive field due to the nitro-group, which hinders the entrance of a cation. Nitrobenzene does not undergo Friedel-Crafts reactions. (80)

7.2. The System Nitrobenzene + Sulfur Dioxide + Chlorine

This reaction was studied with the gas-liquid reactor. Several runs were made at 12, 25 and 50°C, an SO_2/Cl_2 ratio of 2/1, gas feed rate of 2.5 l/hr, and an average gamma intensity of 3,700 rad/min. The

reaction products were purified by fractional distillation at reduced pressure.

After removal of the more volatile components (SO_2Cl_2 , SO_2 , Cl_2) the remaining nitrobenzene was analyzed for Cl, S and $-\text{SO}_2\text{Cl}$, chemically and also by infrared. The results were again negative.

7.3. The System Benzene + Sulfuryl Chloride

Benzene can be sulfochlorinated directly with sulfuryl chloride and AlCl_3 .⁽⁸¹⁾ This Friedel-Crafts synthesis was duplicated with good yields. To determine whether gamma radiation could be substituted for the AlCl_3 catalyst in this reaction, a mixture containing 35 ml C_6H_6 and 33 ml SO_2Cl_2 was irradiated for 1296 min at a dose rate of 4000 rad/min and a temperature of 10°C . The reaction products were separated by fractional distillation at reduced pressure. The residue, remaining after the removal of unreacted C_6H_6 and SO_2Cl_2 , was found to consist of various chlorinated benzene products, mostly isomers of the full addition product, $\text{C}_6\text{H}_6\text{Cl}_6$. Tests for sulfur were negative, as was the qualitative test for $-\text{SO}_2\text{Cl}$ groups. The infrared spectrum also failed to disclose any sulfonyl chloride groups.

7.4. The System Benzene + Sulfur Dioxide + Chlorine

The study of this system was made with the gas-liquid reactor. Other investigators⁽³²⁾ reported a violent reaction between C_6H_6 and Cl_2 under the influence of gamma radiation. For this reason, the irradiated runs were carried out with solutions of C_6H_6 in CCl_4 (20% by volume). In one experiment, the conditions were as follows:

SO_2/Cl_2 ratio in feed gas: 2/1

Temperature: $18-23^\circ\text{C}$

Gamma Intensity: 3,500 rad/min.

After removal of the volatile components (SO_2 , Cl_2 , SO_2Cl_2 , C_6H_6 and CCl_4) by distillation at reduced pressure, a crystalline residue remained in the still. This residue was washed with benzene, dried and analyzed for Cl, S, and $-\text{SO}_2\text{Cl}$ groups.

Results: Cl - 73.0% (Cl content of $\text{C}_6\text{H}_6\text{Cl}_6 = 73.2\%$)
 S- - less than 0.1%
 $-\text{SO}_2\text{Cl}$ - negative, by color test.

7.5. The System Cyclohexane + Sulfur Dioxide + Chlorine

The successful sulfochlorination of cyclohexane with SO_2 and Cl_2 in the presence of actinic light or other catalysts was reported by several investigators. (25,26,36) There have not yet been any published studies on the sulfochlorination of C_6H_{12} with the aid of gamma radiation. The selection of cyclohexane was prompted by the equivalence of all hydrogen atoms, which excludes the formation of any isomers of the monosulfonyl chloride.

Preliminary experiments of the gamma-induced direct sulfochlorination were quite encouraging. The reaction products were found to consist mainly of $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$, and very small amounts of $\text{C}_6\text{H}_{10}(\text{SO}_2\text{Cl})_2$ and $\text{C}_6\text{H}_{11}\text{Cl}$. In a typical exploratory experiment, a total of 6.10 g SO_2 and 3.34 g Cl_2 (molar ratio 2/1) were bubbled for 90 minutes through 30 ml C_6H_{12} at an average gas rate of 0.1 g/min, a temperature of $12-14^\circ\text{C}$, and a gamma radiation intensity of 2,520 rad/min. The residue left after removal of volatile components by distillation at 10 mm Hg weighed 2.1 g, which corresponds to a conversion of 24.4% based on Cl_2 , the limiting reactant. (Considerably better yields were obtained later, when the reactor head was modified to reduce losses by foaming and the purification equipment was provided with an entrainment separating column.)

The purification of $C_6H_{11}SO_2Cl$ by fractional distillation was quite difficult, because of the thermal instability of this compound. When heated, cyclohexanesulfonyl chloride decomposes in accordance with the following equation:

Thus, the "purified" product always contained small amounts of $C_6H_{11}Cl$.

The difficulty of purifying $C_6H_{11}SO_2Cl$ by distillation was already encountered by Borsche and Lange, who were the first to synthesize this compound in the following manner:⁽⁸⁾

For the determination of physical and chemical properties, it was possible to distill small amounts of $C_6H_{11}SO_2Cl$ at a pressure below 0.5 mm Hg.

The properties of the compound synthesized with gamma radiation and purified as described above were as follows:

Hydrolyzable Cl:	Found 19.2%	Calculated:	19.41%
Total Cl :	" 19.6%	"	19.41%
Total S :	" 17.3%	"	17.55%.

Qualitative color test for $-SO_2Cl$ (p-toluidine - pyridine): positive.

Infrared spectrum: characteristic absorption peaks for the SO_2Cl group at 1374 and 1160 cm^{-1} .

Sp. Gr. 25/4: 1.23

B.P. at 15 mm Hg: $125-127^\circ C$ [Ref. (5): $127-8^\circ C$]

Refr. index at $25^\circ C$: 1.4948.

The identity of the cyclohexanesulfonyl chloride was further confirmed by preparation of a derivative, cyclohexanesulfonanilid, which has a M.P. of 87°C . The derivative was prepared by reacting the sulfonyl chloride in absolute alcohol with an equivalent amount of aniline, followed by extraction with ether.⁽⁸⁾ The sulfonanilide or the sulfontoluide derivatives can also be prepared by the Hinsberg reaction.⁽⁷⁴⁾

The reaction products contained a small amount of white crystals, insoluble in cyclohexane. The chemical composition of these crystals corresponded to cyclohexane disulfonyl chloride (Cl - 25.2% and S - 22.8%). From the low solubility of this compound in C_6H_{12} , it would appear to be the 1,4 isomer, which, upon heating, decomposes into SO_2 and 1,4-dichlorocyclohexane with a M.P. of 102°C .⁽²⁶⁾

Cyclohexanesulfonyl chloride is not commercially available now; if manufactured economically, it could become an important intermediate in the manufacture of sulfonic acids (useful as surface-active agents) by hydrolysis, esters (e.g., ethyl-, butyl- and hexadecyclohexanemonosulfonate have been cited as plasticizers for cellulose derivatives and other plastics) by reaction with alcohols, amides (useful as plasticizers and insecticides) by reaction with amines, etc.

The cyclohexanedisulfonyl chloride, particularly the 1,4 isomer, which can be produced by gamma irradiation in fair yields under certain operating conditions, may be of considerable value as a monomer in the manufacture of synthetic fibers and plastics of the condensation type, because of its two reactive functional groups. The system $\text{C}_6\text{H}_{12}/\text{SO}_2/\text{Cl}_2$ was selected for more detailed study. The results of the process and kinetics investigations are presented in the following two sections.

8. Process Investigation of Direct Sulfochlorination of Cyclohexane

In the course of the preliminary investigations of the sulfochlorination of hydrocarbons induced by gamma radiation, only the synthesis of cyclohexanesulfonyl chloride from cyclohexane, sulfur dioxide and chlorine warranted any further study. It became immediately apparent that this was a chemical chain reaction proceeding at very high rates, and that one approach would be needed for the study of the effects of process variables on selectivity and conversion and another one for the study of the kinetics of the reaction.

8.1. Objective

The objective of a process investigation is to obtain experimental data needed for the design of process equipment and its operation at optimum conditions.

Frequently, process data obtained in the laboratory were found to be of little value in the actual design of reactors. In a recent analysis of reactor design methods, Chu⁽¹⁵⁾ pointed out the difficulty of interpreting laboratory data consisting of a number of graphs, showing isolated effects of temperature, pressure, space velocity and reactant ratios on the yield of a specified product. Such information has limited value for the design of reactors, because it fails to express quantitatively interactions between various factors.

For the gamma-induced sulfochlorination of cyclohexane the process investigation consisted of determining the significance of the effect of major factors (temperature, radiation intensity, composition of feed) on product selectivity and conversion. This study was carried out as a factorial experiment, at three levels for each of the independent variables cited above. Another important variable, the gas feed rate, was held

constant because the type of reactor used and the pronounced foaming of the liquid severely limited the rate at which the SO_2/Cl_2 feed could be bubbled through the reactor.

The advantage of a factorial experiment is that the effects of a number of different factors are investigated simultaneously, since the scheme contains all combinations that can be formed from the different factors.

By carrying out an analysis of variance it becomes possible to estimate, not only the significance of independent factors, but also any interactions that exist. The results may not be sufficient to establish with a high degree of precision the optimum combination of factors which would give the highest conversion or the best selectivity for a given process. Box and Wilson⁽¹⁰⁾ have developed a special approach for studying the nature of the response in the neighborhood of the maximum. However, the results derived from the present process study have fulfilled the main objectives, namely, to determine the relative significance of the effects of temperature, SO_2/Cl_2 ratio and gamma intensity on conversion and selectivity, and to supply basic information for an economic estimate for the sulfochlorination of cyclohexane induced by gamma radiation.

8.2. Experimental Procedure

The equipment used for this study was the gas-liquid reactor and accessories described in Section 4.

Before each run, the glass reactor was thoroughly cleaned with acetone, rinsed with cyclohexane, and pumped out to a pressure of less than 0.1 mm Hg. All supply and withdrawal lines were also first evacuated and then flushed for at least 15 minutes with nitrogen. While maintaining a slight positive N_2 pressure on the gas inlet side, 20 ml of cyclohexane

were introduced in the reactor; the reactor was closed and brought up to the desired temperature by circulating water of closely controlled temperature through the outer jacket. The two metering cylinders were filled with Cl_2 and SO_2 from the respective liquefied gas cylinders. With the valves arranged so as to by-pass the reactor, the flow rates of each gas were adjusted with needle valves to a predetermined rate, as shown by bubblers filled with concentrated sulfuric acid. The resistance of the by-pass line was adjusted to match the total resistance of reactor feed and withdrawal lines ($1/2$ to $3/4$ in. Hg). After the desired gas flow rate was obtained for each gas, the flow through the by-pass branch was continued for an additional 15 min. At the end of this period, the gas feed was diverted to the reactor and an electric timer was started (time = 0). For the gas flow rates used (2.3 l/hr), about 10 min were required for the SO_2/Cl mixture to reach the reactor. During this time interval, the reactor was placed in the aluminum urn and the water-tight aluminum cover closed by means of an expansion fitting. After 15 min (time = 15), the urn was lowered into the irradiation site. Slight adjustments of the needle valves controlling the gas flow were necessary during the run, particularly as the gas pressure in the metering cylinders dropped. Pressure readings for each cylinder were taken every five minutes, and the rate of pressure decrease was used as a guide for regulating the gas flow and thus maintain a rather uniform feed rate.

Other data obtained during a run were: reactor temperature, static pressure upstream and downstream of the reactor, and flow rates through the two bubblers (downstream of the reactor) before and after the caustic absorbers. These latter flow rates were an approximate indication for the start of the reaction and the extent of the conversion.

One or two minutes after the start of irradiation, a rather violent reaction occurred at high radiation intensities between the dissolved SO_2 and Cl_2 and C_6H_{12} which raised the temperature instantaneously by as much as 8°C . However, during the rest of the run the temperature was controlled to within better than $\pm 0.5^\circ\text{C}$. Seventy five minutes after the start of the irradiation (time = 90), the Cl_2 and SO_2 metering tanks were closed, the respective pressures recorded, and the flow of N_2 started at a rate equal to the total gas flow rate during the preceding period. In this manner, the entire amount of metered gas was swept through the reactor by the N_2 stream. After an additional 15 min (time = 105), the urn was removed from the pool, the contents of the reactor were brought up to room temperature and transferred to a tared 50-ml round bottom distilling flask with a 24/40 standard taper ground neck and stopper. The reactor as well as the flask were wrapped in aluminum foil, and the transfer was done in subdued light to prevent any photochemical reaction. One major difficulty during the first few runs was the excessive foaming of the cyclohexane when gases were bubbled through it. This resulted in appreciable losses of material during these runs, giving erroneous conversion figures. This was remedied by enlarging the top of the reactor to act as an entrainment trap. The results from the first 12 experiments (Nos. 34-45) were discarded, because of the obviously erroneous conversion figures. The products were subjected to fractional distillation to remove unreacted SO_2 , Cl_2 , C_6H_{12} and also some SO_2Cl_2 and HCl found during the reaction. The bulk of these materials were boiled off at 40-45 mm Hg and a still temperature not exceeding 40°C . The pressure was then lowered to 20 mm Hg to remove the last traces of C_6H_{12} . The flask and contents were weighed, to obtain the total product weight. This product was then

analyzed for total chlorine, hydrolyzable chlorine and in some cases for total sulfur. All analyses were run in duplicate and a third determination was made if the first two results differed by more than 1.5%. The non-hydrolyzable chlorine contents were obtained by difference. To determine the exact amounts of metered Cl_2 and SO_2 , it was necessary to obtain the exact capacities of the two metering systems (cylinders + piping) and the gas densities for the range of room temperatures encountered.

Volume of SO_2 system:

Volume of N_2 (STP) removed for one psi decrease in pressure = 89.7 ml.

This corresponds to

$$\frac{89.7}{22,400} = 0.004 \text{ g-mole } \text{N}_2$$

$$V = \frac{RT (n_1 - n_2)}{P_1 - P_2} = \frac{1205.6 \times 297 \times 0.004}{1} = 1,432 \text{ ml.}$$

Volume of Cl_2 system:

$$V = \frac{1205.6 \times 296 \times 159.8}{22,400 \times 1} = 2,545.6 \text{ ml.}$$

Densities as a function of pressure and temperature were obtained for SO_2 from thermodynamic tables⁽⁶⁸⁾ and were calculated for Cl_2 from the following equation of state:⁽⁴¹⁾

$$V = RT/P + 39 - \frac{8.5 \times 10^8}{T^{2.6}} .$$

Working curves were prepared giving the weight in grams of the gas in each system as a function of pressure and ambient temperature.

Two runs (Nos. 46 and 70) were carried out without any gamma radiation. The products did not contain any sulfonyl chlorides, which

shows that the "dark reaction" is entirely negligible. A complete material balance was carried out for run No. 47, to ascertain the validity of the equation representing the over-all reaction:

The procedure, outlined diagrammatically in Figure 10, was as follows:

The irradiated run was carried out as described in Section 7.2, except that all off-gases were scrubbed through CCl_4 maintained at -15°C with a dry ice-isobutanol bath. The volume of C_6H_{12} introduced in the reactor was measured and the amounts of SO_2 and Cl_2 charged were obtained from the pressure readings. After the termination of the run, N_2 was bubbled through the reactor for 30 minutes to remove dissolved HCl , SO_2 and Cl_2 . The concentration of free Cl_2 absorbed in CCl_4 was obtained from the optical absorbance at $4000 \text{ \AA}$ and the calibration curve in Figure 9. Aliquots of the CCl_4 solution were extracted with an aqueous solution of NH_3 (2.5%) and H_2O_2 (1.0%). The extract was boiled, and chloride and sulfate determined volumetrically as described in Section 5.1.5. The HCl content was obtained by subtracting from the total chloride concentration an amount of chloride equivalent to the free Cl_2 , previously determined spectrophotometrically. The reaction products were distilled under reduced pressure and the residue was weighed. After filtering off the small insoluble fraction of $\text{C}_6\text{H}_{10}(\text{SO}_2\text{Cl})_2$, the liquid was analyzed for total Cl , hydrolyzable Cl , and total S . From this it was possible to calculate the amounts of $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ and $\text{C}_6\text{H}_{11}\text{Cl}$ in the product. The distillate overhead, consisting mainly of C_6H_{12} , was weighed, and the SO_2Cl_2 contents were determined by titration with NaOCH_3 .

Figures shown are mmoles

FIGURE 10. ANALYTICAL PROCEDURE FOR THE MATERIAL BALANCE DURING THE SULFOCHLORINATION OF CYCLOHEXANE

The results of the final material balance are summarized below:

<u>Reactant</u>	<u>Charged</u>	<u>Accounted for</u>		<u>Lost</u>	
	mmoles	mmoles	%	mmoles	%
C ₆ H ₁₂	185.5	183.7	99.0	1.8	1.0
Cl ₂	46.5	45.9	98.7	0.6	1.3
SO ₂	93.6	91.7	98.0	1.9	2.0

The stoichiometric balance for the main reaction is summarized below:

<u>Material</u>	<u>Amount Reacted</u> [*] mmoles	<u>Amount Produced</u> mmoles
C ₆ H ₁₂	41.3	-
Cl ₂	41.3	-
SO ₂	42.0	-
C ₆ H ₁₁ SO ₂ Cl	-	39.0
HCl	-	40.1

8.3. Experimental Results

All experimental and calculated results are summarized in Table VIII.

The conversion figures were based on the reactant in limiting concentration. For instance, in Run No. 47 the total product weight (after removal of unreacted C₆H₁₂, SO₂, Cl₂, and SO₂Cl₂ and HCl formed during the reaction) was 8.04 g. The hydrolyzable chlorine (17.22%) was present only as part of the -SO₂Cl group. The moles of C₆H₁₁SO₂Cl produced were calculated as follows:

$$\text{moles C}_6\text{H}_{11}\text{SO}_2\text{Cl} = \frac{17.22}{100} \times 8.04 \times \frac{182.7}{35.5} \times \frac{1000}{182.7} = 39.0 \times 10^{-3},$$

*Includes materials lost or used up in minor side-reactions.

where

$$\text{M.W. of } \text{C}_6\text{H}_{11}\text{SO}_2\text{Cl} = 182.7$$

$$\text{A.W. of Cl} = 35.5$$

The theoretical yield being 46.5 mmoles (equivalent to Cl_2 charged), the conversion equals $\frac{39.0}{46.5} \times 100 = 83.9\%$.

There are two competing reactions during the direct sulfochlorination of a hydrocarbon:

The chlorination reaction is an undesirable side-reaction in this case, and the relative ratio of chlorinated to sulfochlorinated product is a measure of the selectivity of the reaction.

The fraction of sulfochlorinated cyclohexane in the purified product is indicated by the content of hydrolyzable chlorine or sulfur. It was shown that sulfur and hydrolyzable chlorine were present in equivalent amounts; consequently, the fraction of sulfochlorinated product could be obtained from the hydrolyzable chlorine content only. In the illustrated case $\text{Cl}_{\text{Hydrolyz.}}$ amounted to 17.22%. The non-hydrolyzable chlorine content ($\text{Cl}_{\text{N.h.}}$), obtained as the difference between total chlorine and hydrolyzable chlorine, was in this case

$$\text{Cl}_{\text{N.h.}} = 17.43 - 17.22 = 0.21\%$$

The selectivity index was arbitrarily selected as the ratio $\text{Cl}_{\text{N.h.}}/\text{Cl}_{\text{H}}$:
For the illustrated run

$$\text{Cl}_{\text{N.h.}}/\text{Cl}_{\text{H}} = 0.21/17.22 = 0.012.$$

A high degree of selectivity for sulfochlorination is indicated by a small value of the selectivity index, while an increasing degree of chlorination is reflected by a large selectivity index. In Figure 11, selectivity indices are plotted against feed gas compositions, with gamma-radiation intensity as a second parameter.

In radiation chemistry it is important to estimate yields as a function of absorbed radiation energy. The gamma dose rate, measured with the ferrous sulfate dosimeter, is expressed in rad/min referred to pure water. In the present reaction, cyclohexane was by far the major constituent of the irradiated liquid and, therefore, the dose rate was recalculated to indicate the corresponding dose rate for pure C_6H_{12} .

For the range of photon energies from this gamma source and for the type of irradiated substances the absorption coefficients for two materials are in the same ratio as the respective electron densities, as was shown in Section 5.4.1. The electron densities for cyclohexane and water are, respectively, 2.66×10^{23} and 3.33×10^{23} electrons per cc. To convert the absorbed dose rate from water to cyclohexane one multiplies by the ratio of the volumetric electron densities; in the illustrated case

$$\text{Dose Rate } (C_6H_{12}) = 7,300 \times \frac{2.66 \times 10^{23}}{3.33 \times 10^{23}} = 5,830 \text{ rad/min.}$$

The radiochemical yield G can now be calculated from the amount of cyclohexanesulfonyl chloride formed and the absorbed gamma energy.

The weight of $C_6H_{11}SO_2Cl$ formed, obtained from the total weight of purified product and the hydrolyzable chlorine content, was shown previously to be 39.0 mmoles for the illustrated example, which corresponds to

$$39.0 \times 10^{-3} \text{ moles} \times 6.02 \times 10^{23} \frac{\text{molecules}}{\text{moles}} \times \frac{1}{20} \frac{1}{\text{cc}} = 1.17 \times 10^{21} \text{ molecules}$$

of $C_6H_{11}SO_2Cl$ per cc of irradiated liquid.

FIGURE II. SELECTIVITY OF SULFOCHLORINATION OF CYCLOHEXANE

The rad has been defined as the amount of absorbed radiation energy equivalent to 100 ergs per gram. The duration of the run being 90 minutes, the total absorbed energy per cc of cyclohexane was

$$90 \text{ min} \times 5.830 \times 10^3 \frac{\text{rad}}{\text{min}} \times 10^2 \frac{\text{erg}}{(\text{g})(\text{rad})} \times 6.24 \times 10^{11} \frac{\text{ev}}{\text{erg}} \\ \times 0.774 \frac{\text{g}}{\text{cc}} = 2.53 \times 10^{19} \frac{\text{ev}}{\text{cc}} .$$

The radiochemical yield was $G_{\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}} = \frac{1.17 \times 10^{21} \times 10^2}{2.53 \times 10^{19}} = 4,630$

molecules produced per 100 ev of absorbed energy. For the entire series of runs (except No. 51) the calculation of the G number simplifies to

$$G_{\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}} = 1.96 \times 10^5 \frac{W \times P}{I},$$

where

W = Total weight of purified product, g

P = Hydrolyzable chlorine content, %

I = Gamma dose rate, rad (C_6H_{12})/min.

Figure 13 shows the relation between the radiochemical yield of $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ and the radiation intensity.

The average chain length n for this chain reaction is given by

$$n = \frac{G_{\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}}}{G_R},$$

where G_R is the radiochemical yield for the formation of free radicals.

In the present system, by far the largest part of free radicals were produced by the radiolysis of cyclohexane, since the concentration of all other ingredients was very small.

A G_R of 8.8 was reported for cyclohexane,⁽⁹⁾ from which apparent chain length values of about 500 and 250,000 were calculated for dose rates of 5,800 and 3.97 rad/min, respectively.

Under the experimental conditions of the present series of runs, the calculated values for the average chain length may be somewhat low. Schuler⁽⁷¹⁾ has found that the presence of solutes which have high electron affinities, e.g., sulfur dioxide, decrease by about 40% the hydrogen yield and consequently also G_R , the yield of free radicals for the gamma irradiation of cyclohexane. The decrease in free radicals yield is believed to be due to a transfer of energy to the solute by an electron-capture mechanism.

Average reaction rates were calculated as illustrated for Run No. 48:

Weight of product: 9.50 g

Hydrolyzable chlorine: 17.50 %

$$\text{Yield of } C_6H_{11}SO_2Cl: \frac{17.50}{100} \times 9.50 \times \frac{182.7}{35.5} = 8.56 \text{ g}$$

$$\text{or } \frac{8.56}{182.7} = 46.9 \text{ mmoles.}$$

For an original C_6H_{12} volume of 20 ml and an irradiation period of 90 min, one obtains an average reaction rate of

$$46.9 \times \frac{1000}{20} \times \frac{1}{90} = 26.1 \frac{\text{mmoles}}{(\text{liter})(\text{min})} .$$

The results for all runs at a temperature of 11.5°C and an SO_2/Cl_2 ratio of 2/1 are presented in Figure 12.

8.4. Statistical Analysis of Experimental Results

The process study of the sulfochlorination of cyclohexane was carried out as a 3 x 3 x 3 factorial experiment. The independent variables were:

FIGURE 12. REACTION RATES FOR THE SULFOCHLORINATION OF CYCLOHEXANE

FIGURE 13. RADIOCHEMICAL YIELDS
FOR SULFOCHLORINATION
OF CYCLOHEXANE

Temperature, °C:

$$T_1 = 11.5 \quad T_2 = 25.0 \quad T_3 = 40.0$$

Gamma Radiation Intensity, rad (H₂O)/hr:

$$F_1 = 82(79-86) \quad F_2 = 546(515-628) \quad F_3 = 6,560 (6,000-7,300)$$

Ratio of SO₂/Cl₂, moles/moles:

$$R_1 = 2.0 \quad R_2 = 1.0 \quad R_3 = 0.5.$$

The selection of levels for the independent variables is somewhat speculative in the case of a process about which little or no preliminary information is available. The assignment of levels is sometimes dictated by limitations of the experimental equipment or the properties of the chemical system. This was the case for the choice of temperatures in the present study: 11.5° was the lowest reactor temperature which could be maintained with the available refrigeration equipment, while 40.0°C was the highest temperature at which the vapor pressure of cyclohexane was still sufficiently low to avoid excessive loss by vaporization. The temperature of 25°C was in the middle of the range.

The ratios of SO₂/Cl₂ were selected arbitrarily on both sides of the equimolar ratio which corresponds to the stoichiometric relation.

The selection of levels for the gamma-radiation intensities was based on radiochemical yields reported in the literature for other chain reactions. Even though the levels were varied by one order of magnitude, the results obtained showed that the chosen gamma intensities were too high by a factor of ten. Nevertheless, the difference between the results obtained for F₁ and F₂ were sufficiently large to point out the significance of this factor and to indicate the direction for supplementary runs.

The dependent variables were:

Selectivity of reaction = chlorination/sulfochlorination

$$= \text{Cl}_{\text{Non-hydrol.}} / \text{Cl}_{\text{Hydrolyzable}}$$

Conversion to $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ = percent of theoretical conversion,

based on the amount of limiting reactant.

The experimental results are summarized in Tables I and II. An analysis of variance was carried out for both dependent variables, following the procedure outlined by Brownlee.⁽¹³⁾

First, three two-way tables were formed by summing over each of the three variables in turn. These two-way tables contained the sums of squares and the mean squares for each factor and also the two-way interactions between the independent variables. The final analysis of variance table was compiled from the three two-way tables and the "total variance" was obtained from all individuals. The results, both before and after pooling of the non-significant factors, are presented in Tables III, IV, V, and VI.

The results of the statistical analysis can be summarized as follows:

For a constant molar rate of gas feed, the selectivity of sulfochlorination is very significantly affected by the SO_2/Cl_2 ratio in the feed gas, by the gamma intensity, and also by the interaction of these two factors. The selectivity is independent of temperature, within the range studied, and there does not seem to be any effect due to an interaction between temperature and the two other independent variables.

Only the gamma intensity was found to have a significant effect on the conversion to $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$, within the range of variables studied.

Table I

Sulfochlorination of Cyclohexane
Factorial Experiment - Selectivity Data

R	T, °C	$F_1 = 82 \text{ rad/min}$	$F_2 = 546 \text{ rad/min}$	$F_3 = 6560 \text{ rad/min}$
$R_1 = 2:1$	$T_1 = 11.5$	0.13	0.01	0.01
	$T_2 = 25.0$	0.14	0.01	0.03
	$T_3 = 40.0$	0.21	0.02	0.02
$R_2 = 1:1$	$T_1 = 11.5$	0.40	0.14	0.12
	$T_2 = 25.0$	0.42	0.16	0.20
	$T_3 = 40.0$	0.47	0.24	0.17
$R_3 = 1:2$	$T_1 = 11.5$	2.01	0.93	1.30
	$T_2 = 25.0$	2.17	1.36	0.74
	$T_3 = 40.0$	1.96	1.20	1.36

Figures shown are ratio of non-hydrolyzable chlorine to hydrolyzable chlorine.

Table II

Sulfochlorination of Cyclohexane
Factorial Experiment - Conversion Data

R	T, °C	F ₁ = 82 rad/min	F ₂ = 546 rad/min	F ₃ = 6560 rad/min
R ₁ = 2:1	T ₁ = 11.5	86	92	92
	T ₂ = 25.0	81	89	81
	T ₃ = 40.0	70	90	93
R ₂ = 1:1	T ₁ = 11.5	34	73	77
	T ₂ = 25.0	19	73	83
	T ₃ = 40.0	22	67	54
R ₃ = 1:2	T ₁ = 11.5	53	80	97
	T ₂ = 25.0	35	64	95
	T ₃ = 40.0	47	73	96

Figures shown are conversion to C₆H₁₁SO₂Cl, expressed as % of theoretical conversion based on the reactant of limiting concentration.

Table III
Sulfochlorination of Cyclohexane
Analysis of Variance - Selectivity Results

<u>Source of Variance</u>	<u>Degrees of Freedom</u>	<u>Sums of Squares</u>	<u>Mean Squares</u>
Between R	2	10.1012	5.0506***
Between T	2	0.0211	0.0105 N.S.
Between F	2	1.1275	0.5637**
R x T Interaction	4	0.0046	0.0012 N.S.
T x F Interaction	4	0.0865	0.0216 N.S.
F x R Interaction	4	0.6630	0.1657*
Residual	8	0.2557	0.0320
Total	26	12.2596	

Variance Ratios

Between R:	157.83	F _{.001} (2,8) = 18.5	F _{.001} (4,8) = 14.4
Between F:	17.62	F _{.01} (2,8) = 8.65	F _{.01} (4,8) = 7.01
F x R Interaction:	5.18	F _{.05} (2,8) = 4.46	F _{.05} (4,8) = 3.84

N.S. Probability P of variation being due to chance in greater than 5%.

* $1\% < P \leq 5\%$

** $0.1 < P \leq 1\%$

*** $P \leq 0.1\%$

Table IV
Analysis of Variance - Selectivity Results
 (After Pooling)

<u>Source of Variance</u>	<u>Degrees of Freedom</u>	<u>Sums of Squares</u>	<u>Mean Squares</u>	<u>Components of Variance</u>
Between R	2	0.1012	5.0506***	$9 \sigma_R^2 + 3 \sigma_{fr}^2 + \sigma_O^2$
Between F	2	1.1275	0.5637***	$9 \sigma_F^2 + 3 \sigma_{fr}^2 + \sigma_O^2$
F x R Interaction	4	0.6630	0.1657***	$3 \sigma_{fr}^2 + \sigma_O^2$
Residual	18	0.3679	0.0204	σ_O^2
<hr/>				
Total	26	12.2596		
<hr/>				
<u>Variance Ratios</u>				
Between R:	247.58	$F_{.001} (2,18) = 10.4$	$\sigma_O^2 = 0.0204$	
Between F:	27.63		$\sigma_{fr}^2 = 0.0485$	
F x R Interaction:	8.12	$F_{.001} (4,18) = 7.5$	$\sigma_F^2 = 0.0442$	
			$\sigma_R^2 = 0.5440$	

Table V
Sulfochlorination of Cyclohexane
Analysis of Variance - Conversion Results

<u>Source of Variance</u>	<u>Degrees of Freedom</u>	<u>Sums of Squares</u>	<u>Mean Squares</u>
Between R	2	20.55	10.27
Between T	2	1.75	0.87
Between F	2	31.90	15.95
R x T Interaction	4	0.65	0.16
T x F Interaction	4	0.25	0.06
F x R Interaction	4	5.05	1.26
Residual	8	76.36	9.54
Total	26	136.51	

Note: All original figures were divided by 10.

Table VI
Sulfochlorination of Cyclohexane
Analysis of Variance - Conversion Results
(After Pooling)

Source of Variance	Degrees of Freedom	Sums of Squares	Mean Squares	Components of Variance
Between R	2	20.55	10.27 N.S.	$9\sigma_R^2 + \sigma_O^2$
Between F	2	31.90	15.95 *	$9\sigma_F^2 + \sigma_O^2$
Residual	22	84.06	3.82	σ_O^2
Total	26	136.51		

Variance Ratios

Between R: 2.7	F.05 (2,22) = 3.4	$\sigma_O^2 = 3.82$
Between F: 4.2	F.01 (2,22) = 5.7	$\sigma_F^2 = 1.35$
		$\sigma_R^2 = 0.72$

Note: All original figures were divided by 10.

8.5. Interpretation of Results

The reaction of cyclohexane with SO_2 and Cl_2 in the presence of gamma radiation is a chemical chain reaction proceeding at very high rates. Sulfochlorination is the predominant reaction and chlorination occurs only to a very small extent. In addition to cyclohexanesulfonyl chloride, the reaction products contained small amounts of cyclohexanedisulfonyl chloride and chlorocyclohexane.

The rate of sulfochlorination was found to be about 5 to 100 times higher than the rate of chlorination, for an excess of SO_2 in the feed gas and a gamma intensity from 82 to 6500 rad (H_2O)/min. Kharasch and co-workers⁽⁴⁶⁾ proposed the following mechanism for the photochemical sulfochlorination of aliphatic hydrocarbons:

Reaction (3a) explains the formation of the chlorinated product, by the reaction of an alkyl radical and chlorine. This reaction competes with the sulfochlorination reaction (3b), but, under the conditions studied, chlorination takes place to a much lesser extent than sulfochlorination.

A comparison of the photochemical and gamma-induced reactions reveals a number of similarities.

Kroepelin and co-workers⁽⁴⁹⁾ have found that during the sulfochlorination of hydrocarbons with SO_2 and Cl_2 in the presence of ultra-

violet light, the reaction rate increases up to a certain value of the intensity of the incident light, but remains constant for further increases in light intensity. Identical results were obtained during the gamma-induced reaction. Other similarities are: at lower light intensities (corresponding to lower gamma intensities) the reaction rate decreases and the selectivity deteriorates; the selectivity of both reactions improves with an increase in SO_2/Cl_2 ratio; both reactions are strongly inhibited by oxygen which is believed to act as a chain-terminating agent.

Kroepelin reported that an increase in temperature from 25 to 50°C caused a deterioration of the selectivity index from 0.2 to 0.45. The results of the present study have shown that temperature does not significantly affect the selectivity of the reaction, within the range covered (11.5 to 40°C). In general, the selectivity of the gamma-induced reaction is much better than that of the photochemical reaction.

Very few quantitative results have been published on the photochemical sulfochlorination of cyclohexane. The following data are based on the patent disclosures of Fox:⁽²⁶⁾

Light intensity	Not specified
SO_2/Cl_2 molar ratio	1.4/1.0
Gas feed rate	9 g/min = 180.6 l/hr
Temperature	25 to 72°C
C_6H_{12} at start of reaction	6,000 g = 71.0 moles
SO_2 supplied	8,602 g = 134.4 moles
Cl_2 supplied	7,242 = 101.9 "
$\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ recovered	5,273 = 28.9 "
$\text{C}_6\text{H}_{10}(\text{SO}_2\text{Cl})_2$ "	1,523 = 5.4 "

$C_6H_{11}Cl$ recovered	Not given
Duration of reaction	30 hours
Average rate	$2.26 \times 10^{-4} \frac{\text{moles } C_6H_{11}SO_2Cl}{(\text{mole } C_6H_{12})(\text{min})}$
Conversion to $C_6H_{11}SO_2Cl$ based on Cl_2 supplied	28%

The conversion for comparable conditions for the gamma-induced reaction ranges from about 50 to 92% (based on Cl_2 supplied) and the rate of formation of $C_6H_{11}SO_2Cl$ for a dose rate of 100 rad (C_6H_{12})/min is $2.72 \times 10^{-3} \frac{\text{moles } C_6H_{11}SO_2Cl}{(\text{mole } C_6H_{12})(\text{min})}$.

From this comparison, it follows that the rate of the gamma-induced chlorination is about 10 times higher than the rate of the comparable photochemical reaction.

The deterioration of the selectivity at lower radiation intensities can be explained as follows: Chlorination proceeds in accordance with reaction (3a) and the rate is proportional to the concentration of chlorine. The consumption of Cl_2 is determined predominantly by reaction (4), which produces the sulfonyl chloride. At higher radiation intensities, sulfochlorination proceeds so rapidly that the stationary concentration of Cl_2 is extremely small, which in turn suppresses the chlorination reaction. At lower radiation intensities, chlorine is supplied faster than it can be consumed by reaction (4), and this excess of chlorine becomes available for the chlorination reaction (3a). The over-all result is a deterioration of the selectivity of the reaction.

The similarities between the photochemical and gamma-induced sulfochlorination reactions suggest that the chain-propagating steps, [reactions (2), (3b) and (4)] are the same in both cases.

The initiation reaction is certainly different. The photochemical reaction is initiated by the dissociation of a chlorine molecule into two chlorine atoms or free radicals, following the absorption of one quantum of light. This is in accordance with the Einstein law of photochemical equivalence. Indeed, Kroepelin⁽⁴⁹⁾ found that if the incident light was first filtered through a saturated solution of Cl_2 in CCl_4 and an aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$, there was no detectable sulfochlorination reaction.

It is unlikely that the chain reaction occurring under gamma radiation is initiated to any significant extent by the radiolysis of Cl_2 , since the very low concentration of Cl_2 could account for only a very small fraction of the free radicals produced by gamma radiation. In addition, Henglein and Url⁽³⁷⁾ have pointed out that if the gamma-induced sulfochlorination of hydrocarbons were initiated only by the radiolysis of Cl_2 , the resulting chain lengths would be of the order of 10^9 , which is considered too high for a chemical chain reaction.

Cyclohexane is the main component of the reaction mixture. Quantitative data for the number of free radicals produced during the gamma irradiation of C_6H_{12} are summarized below:

<u>Method of Measurement</u>	<u>G_R</u>	<u>Reference</u>
Initiation of styrene polymerization	2.6*	(9)
Initiation of methyl-methacrylate polymerization	6.3*	(9)
Scavenging with DPPH	8.8	(9)
Determination of H_2 formed	10.0**	(71)

All yield figures were corrected to a $G_{\text{Fe}^{+++}} = 15.6$, used in the present study.

* Results considered unreliable by the authors because of certain experimental complications.

** Based on the assumption $G_R = 2 G_{\text{H}_2}$

Chain lengths ranging from 500 to 250,000, calculated from a G_R value of 8.8, are comparable to those reported for similar reactions. (37)

The termination of the chain could occur by one of the following three reactions, in addition to possible interactions between the free radicals and the glass wall or minor impurities:

Reaction (5) is believed to be the mode of termination for the photochemical sulfochlorination. However, the results of the kinetics study of the gamma-induced sulfochlorination in CCl_4 which are described in Section 9 suggest a termination by reaction (6).

The sulfochlorination of cyclohexane with SO_2 and Cl_2 in the presence of gamma radiation is believed to proceed by the following chain mechanism:

Initiation:

($\text{R}^\bullet$ is either $\text{C}_6\text{H}_{11}^\bullet$ or $\text{H}^\bullet$)

Propagation:

Termination:

The results presented in Figure 12 show that, for dose rates below 40 rad/min, the reaction rate is proportional to the square root of the radiation intensity. In this region the initiating reaction (8) appears to be the rate-limiting step.

For rates above 400 rad/min the reaction rate becomes independent of radiation intensity. This would indicate that the reaction rate is now limited by the supply of SO_2 and Cl_2 , an assumption supported by the very high conversion figures in this region. The relatively low values of $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ also indicate that an appreciable number of free radicals formed recombined instead of causing the initiation of a chemical chain reaction.

In the intermediate region (40-400 rad/min) the reaction rate is no longer proportional to the square root of the radiation intensity, but there is also a decrease in conversion. The reaction rate would thus appear to be controlled largely by the gas absorption rate.

8.6. Basic Plant Design Data

A proposed flow-sheet for the large-scale sulfochlorination of cyclohexane with gamma radiation is shown in Figure 14.

The basic features of the reactor are: continuous countercurrent operation, the entering streams being pure liquid C_6H_{12} and a gaseous mixture of SO_2 and Cl_2 ; good agitation and an excess of C_6H_{12} to prevent the formation of $\text{C}_6\text{H}_{10}(\text{SO}_2\text{Cl})_2$, particularly the 1,4 isomer, which is only slightly soluble in C_6H_{12} and may cause a plug-up of the flow system; a gamma source (spent fuel elements, Co^{60} rods, hollow cylinders containing salts of Cs^{137} separated from fission products, etc.) located in the center

FIGURE 14. PLANT FOR SULFOCHLORINATION OF CYCLOHEXANE

of a cylindrical vessel, the liquid in the reactor and the reactor walls providing part of the required shielding; a mechanism for lowering the radiation source into a shielded well, whenever maintenance operations require it.

Sulfochlorination, being a highly exothermic reaction, means must be provided for continuous heat removal, to maintain the liquid in the reactor within a temperature range of 15 to 35°C. A cooling liquid circulating through an outer jacket of the reactor is the preferred mode of heat removal since this provides additional radiation shielding and the mechanical agitation of the fluid in the reactor contributes to good heat transfer. The reactor must be properly shielded for the protection of operating personnel. The liquid stream leaving the reactor consists of unreacted C_6H_{12} , reaction products (mainly $C_6H_{11}SO_2Cl$ and small amounts of SO_2Cl_2 , $C_6H_{11}Cl$ and $C_6H_{10}(SO_2Cl)_2$) and dissolved Cl_2 , SO_2 and HCl . The gas stream leaving the reactor contains unreacted SO_2 and Cl_2 , HCl and also small amounts of entrained C_6H_{12} and SO_2Cl_2 .

In subsequent operations, $C_6H_{11}SO_2Cl$ is separated from the reaction products. First, the more volatile components are removed by flashing or stripping with an inert gas. This is followed by distillation at reduced pressure (about 40 to 60 mm) to remove unreacted cyclohexane which is then recirculated to the reactor.

The more volatile components are condensed by compression and refrigeration and then separated by fractional distillation. SO_2 and Cl_2 are recirculated to the reactor and HCl and SO_2Cl_2 may be recovered as by-products. The fractionation of these products should be relatively simple, in view of the wide spread of their normal boiling points (HCl -85°; Cl_2 -34.6°; SO_2 -10.8; SO_2Cl_2 69.1). The cyclohexanesulfonyl

chloride separated in this manner contains small amounts of $C_6H_{11}Cl$ and $C_6H_{10}(SO_2Cl)_2$, which may not be objectionable for certain applications. However, further purification can be accomplished by conventional methods, the only restriction being a processing temperature below $50^\circ C$, imposed by the thermal instability of $C_6H_{11}SO_2Cl$.

Except for the reactor proper, the equipment required for all other operations of the proposed process is of standard design. The reactor for the radiochemical synthesis contains a number of special features and one design method will be illustrated.

8.6.1. Radiochemical Reactor Design

Above an absorbed dose rate of 200 rad (C_6H_{12})/min, the sulfo-chlorination reaction rate becomes practically independent of radiation intensity (Figure 13). For a uniform conversion rate, the reactor will be designed to provide a dose rate of at least 200 rad/min at the point within the reactor farthest from the gamma source.

Basic design data:

Production rate	$\frac{500 \text{ lb } C_6H_{11}SO_2Cl}{\text{day}}$
Minimum radiation intensity	200 rad (C_6H_{12})/min
Average reaction rate	$0.025 \frac{\text{g-mole } C_6H_{11}SO_2Cl}{(1) (min)}$
Gas feed rate	$1.9 \frac{1}{(min)(1)}$
SO_2/Cl_2 ratio mole/mole	2/1
Conversion, based on Cl_2 supplied	75%
Conversion, based on C_6H_{12} supplied	25%
Maximum gamma intensity outside shielded reactor	$1.75 \frac{mr}{hr} *$

* This figure is based on the presently accepted maximum permissible dose of 300 mr/week. It was calculated for the extreme case of a person stationed continuously outside the shield, 24 hours a day, 7 days a week.

Calculated reactor data:

Reactor volume:

$$\frac{500 \frac{\text{lb}}{\text{day}} \times \frac{1}{24 \times 60} \frac{\text{day}}{\text{min}} \times 454 \frac{\text{g}}{\text{lb}} \times \frac{1}{182.7} \frac{\text{g-mole}}{\text{g}}}{0.025 \frac{\text{g-mole}}{(1)(\text{min})}} = 34.5 \text{ liters.}$$

This volume can be obtained with a cylindrical reactor, 40 cm in diameter, 40 cm high and provided with a hole in the center having a diameter of 20 cm to accommodate the source.

In estimating the size of the required radiation source, the cylindrical reactor can be considered equivalent to a spherical reactor having a radius of 22 cm and provided with a spherical 10-cm radius hole in the center for the radiation source and a cylindrical access to this hole.⁽⁵⁴⁾ Calculations are further simplified by considering the volume of the radiation source to be quite small compared to the volume of the reactor (point source).

If "I" represents the radiation intensity on the periphery of the hole, the radiation at any point within the spherical reactor can be calculated as a function of "I" from the inverse square and the exponential absorption laws for gamma radiation.

The farthest point is 22 cm from the source, the absorption coefficient for $\text{C}_6\text{H}_{12} = 0.06$ and the density of $\text{C}_6\text{H}_{12} = 0.78$. "I" can now be calculated from the requirement that the radiation intensity be at least 200 rad/min (C_6H_{12}) or 250 rad/min (H_2O), which is obtained with a flux of 242 roentgen/min.

$$I \times \frac{10^2}{22^2} \exp (-0.06)(0.78)(12) = 242 \text{ r/min}$$

$$I = 2,050 \text{ r/min} \qquad 123 \text{ kr/hr}$$

An intensity of 123 kr/hr can be obtained from a 3000-curie fission product source, at a distance of 10 cm from its center.⁽⁵³⁾ Allowing for an excess of 100% for various absorption losses, the required source amounts to about 6000 curies.

The thickness for a concrete shielding chamber 4 meters square around the reactor is calculated as follows:

The closest point on the inner wall of the shield is 2 meters from the source; since the gamma intensity is 242 r/min at 22 cm from the source, the intensity at this point will not exceed $\frac{22^2}{200^2} \times 242 \times 60 \times 1000 = 1.75 \times 10^5 \frac{\text{mr}}{\text{hr}}$ disregarding the absorption by the cooling water and the walls of the water jacket. The attenuation factor necessary to reduce this radiation to the permissible maximum of $1.75 \frac{\text{mr}}{\text{hr}}$ is $1.75/1.75 \times 10^5 = 10^{-5}$. This can be accomplished with a concrete shielding (specific gravity 147 lb/ft³) 89 cm thick for a Cs¹³⁷ or a fission product source, or 110 cm thick for a Co⁶⁰ source.⁽⁵⁸⁾

8.6.2. Economic Considerations

An estimate for the total production costs for the manufacture of cyclohexanesulfonyl chloride is considered to be beyond the scope of this study. Furthermore, a cost comparison with a non-radiation process is not possible, since this product is not manufactured commercially now.

The following cost estimate will be limited to the cost component directly attributable to the radiation feature of the process. This includes the radiation source (both initial and replacement costs) and the concrete chamber, but excludes the reactor proper and all other process equipment. The cost figures were obtained from a cost estimate for the production of benzene hexachloride by Martin and co-workers,⁽⁵⁴⁾ but were proportionately adjusted for the different conditions of the present process. The results are shown in Table VII.

Table VII

Radiation Cost Estimate for the Production
of 500 lb/day of $C_6H_{11}SO_2Cl$

	Radiation Source	
	Gross Fission Products, 2 yr.	Cs^{137}
Half-life, years	1.1	33
Total Curies Required - 5 years	23,000	6,000
Selected High Cost, \$/Curie	0.25	2.00
Radiation Cost - 5 years, \$	5,750	12,000
Initial Investment in Radiation Source, \$	1,500	12,000
Radiation Chamber Cost, \$	32,000	32,000
Total Radiation Investment, \$	33,500	44,000
Annual Charges on Radiation Investment at 80% (Depreciation, Taxes, Interest, etc.), \$	26,800	35,200
Annual Radiation Replacement Cost, \$	850	0
Total Annual Radiation Cost, \$	27,650	35,200
Annual Production, 290 Working Days, lb $C_6H_{11}SO_2Cl$	145,000	145,000
Radiation Cost/lb $C_6H_{11}SO_2Cl$, \$	0.19	0.24

A radiation processing cost of about \$0.20 \$/lb $C_6H_{11}SO_2Cl$ may appear somewhat high. However, the very conservative estimates for the radiation cost, particularly in view of the steadily decreasing cost of radiation sources, may alter the calculated processing cost by as much as a factor of 10, in which case this process would definitely become economically attractive. The installation outlined in this Section is sufficiently flexible to permit its use for other processes, which may further improve its over-all economic value.

9. Kinetics of the Direct Sulfochlorination of Cyclohexane in Carbon Tetrachloride

9.1. Objective

The process study of the direct sulfochlorination of cyclohexane with SO_2 and Cl_2 , which was described in Section 8, showed that this reaction proceeds very rapidly under gamma radiation. For SO_2/Cl_2 ratios exceeding 1, sulfochlorination was found to be the predominant reaction, while chlorination occurred only to a small extent.

The procedure used during the process study was not considered adequate for a kinetics study, because of the great rapidity with which this chain reaction proceeded. In addition, it would not have been possible to establish quantitative relations between the rate of reaction and the concentrations of C_6H_{12} , Cl_2 and SO_2 .

Under certain circumstances, kinetics data can be used to explain the mechanism of a reaction, particularly in the case of a chain reaction. The postulation of a reaction mechanism formed another objective of the kinetics study of the sulfochlorination of cyclohexane.

9.2. Experimental Procedure

Reaction rates were determined for dilute solutions of C_6H_{12} in CCl_4 , using a batch reactor. Carbon tetrachloride was selected as the solvent, because of the good solubility in it of all reactants, particularly Cl_2 and SO_2 , and its chemical (but not radiochemical) inertness.

The main features of the equipment used for the sulfochlorination of cyclohexane were described in Section 4. For the kinetics studies, the equipment had to be modified to conform to the following additional requirements:

All reactants be purged of oxygen, either prior to their introduction into the closed reactor system of in situ; slight pressurization with an inert gas during irradiation to prevent any air leakage into the apparatus; accurate metering of small amounts of Cl_2 and SO_2 into the reactor and quantitative absorption of these gases by the liquid in the reactor; means of withdrawing small samples from the reactor, without the introduction of air; protection of the reactor from any extraneous light, to prevent a photochemical reaction; close temperature control, within $\pm 0.5^\circ\text{C}$.

A schematic diagram of the equipment is shown in Figure 15.

Before proceeding with the measurement of reaction rates, it was necessary to confirm the stoichiometric validity of the proposed over-all reaction, namely,

Fifty ml of a solution of C_6H_{12} in CCl_4 (both spectral grade Eastman-Kodak reagents) containing a carefully measured quantity of C_6H_{12} were introduced into the spherical reservoir of the inverted reactor (reservoir at bottom). With water at 1°C circulating through the outer jacket the air was evacuated from the reactor and supply lines, until the liquid started to flash. The system was then filled with argon and the inert gas was swept through the supply lines for five minutes. This was repeated several times, the reactor being finally filled with argon to a pressure of 5 psig. A sample was withdrawn and the actual C_6H_{12} content obtained from a refractive index determination. It was found that repeated flashings did not noticeably alter the C_6H_{12} content, since C_6H_{12} and CCl_4 have very similar vapor pressure curves and the vapor and liquid

FIGURE 15. APPARATUS FOR KINETICS STUDIES

phase compositions are quite close for this binary system.⁽¹⁴⁾ The gas supply valve was closed and the reactor was inverted to its normal position (reservoir on top). The gas metering loop and the supply lines were evacuated to less than 1 mm Hg; an exact quantity of Cl_2 was metered out from the metal loop with the aid of a calibrated pressure gauge and the system filled with argon to maintain a constant pressure of 5 psig. This gas mixture was then bubbled through the liquid in the reactor maintained at 1 to 3°C for exactly 10 minutes at a rate of 80 to 100 bubbles/min. Under these conditions, the gas absorption was found to be quantitative. SO_2 was introduced in a similar manner. The amounts of gas supplied were obtained from the pressure decrease in the respective metering loops. To verify the accuracy of this procedure, the SO_2 content was determined chemically (extracted CCl_4 solution with 2.5% NH_3 , added H_2O_2 to oxidize sulfite to sulfate, boiled to remove excess NH_3 and decompose unreacted H_2O_2 , and then titrated with BaCl_2 , using THQ indicator). The Cl_2 content was found spectroscopically (see Figure 9) and also chemically (extracted with 2.5% NH_3 , boiled to convert any NH_4OCl present into NH_4Cl , titrated with AgNO_3 at a pH of 7.0, using fluorescein as an indicator). Following are some of the results obtained

<u>SO_2 Content in moles/liter</u>	
<u>From Pressure-Volume Measurement</u>	<u>By Chemical Analysis</u>
0.0530	0.0501
0.0792	0.0790
0.0650	0.0664

<u>Cl₂ Content in moles/liter</u>		
<u>From Pressure- Volume Measurement</u>	<u>From Spectroscopic Determination</u>	<u>By Chemical Analysis</u>
0.028	0.0282	0.0279
0.027	0.0274	0.0268
0.015	0.0153	0.0148

Following a short irradiation, the liquid was removed from the reactor, and the various ingredients were determined as follows:

- Cl₂ - spectroscopically
- Cl₂, HCl, SO₂ - flashed over and absorbed in 2.5% NH₃, boiled and determined Cl⁻ and SO₄²⁻ as above. HCl obtained by difference
- C₆H₁₁SO₂Cl - weighed as residue after distilling off C₆H₁₂ and CCl₄ at reduced pressure (10-15 mm Hg).

The results shown in Table XII indicate the stoichiometric conformance with equation (1); an average of 0.93 mole C₆H₁₁SO₂Cl was formed by the disappearance of one mole of Cl₂ due to irradiation.

During the runs for the determination of reaction rates, the reactants were charged as described above. After raising the temperature of the circulating water to the desired point, the reactor was lowered into the irradiation rack with an overhead crane for varying lengths of time (usually one minute). Following the irradiation period, the urn and reactor were brought up to withdraw a sample. Before sampling, the inverted reactor was thoroughly agitated to ensure uniformity. The irradiations were repeated 2 to 4 times, until the Cl₂ concentration became sufficiently low. At first, special precautions were taken to prevent a change of Cl₂ concentrations in the sample by a photochemical reaction, but it appeared that after the contact with air the Cl₂ concentration remained unchanged, even when exposed to ordinary room

illumination for longer periods of time. The Cl_2 concentration at each stage was determined by measuring the absorbance at $4000 \text{ \AA}$. The amount of liquid withdrawn from the reactor for sampling was measured (usually 4 cc) to obtain the volume of liquid remaining in the reactor. This was important, since the gamma flux was not uniform and the average dose received by the liquid in the reactor was dependent on the volume of the liquid. An empirical correction factor, designated as "Volume Dose Factor," was obtained and used in subsequent calculations for the average dose received by the irradiated solution (Figure 16).

It was noted that immediately following the charging of the gases, the Cl_2 concentration decreased slightly. This was probably due to the formation of small amounts of SO_2Cl_2 and some loss of the dissolved Cl_2 by evaporation into the surrounding argon gas. In the temperature range studied, sulfochlorination does not occur without initiation by light, radiation or catalysts, but, for convenience, the over-all decrease in the concentration of Cl_2 not due to irradiation will be designated as "dark reaction" (see Table X and Figure 17). The decrease in Cl_2 concentration due to the dark reaction was deducted from the over-all difference between two consecutive samplings to obtain the net consumption of Cl_2 due to irradiation.

The variables studied in the course of this study were Cl_2 , SO_2 and C_6H_{12} concentrations and the intensity of the gamma radiation at a constant temperature of 25°C . In addition, one run (K-15) was carried out at 35°C , and in another run (K-16) the solution was saturated with oxygen prior to irradiation.

$$\text{V.D.F.} = \frac{\text{ACTUAL AVERAGE DOSE RECEIVED BY THE LIQUID}}{\text{AVERAGE DOSE RECEIVED BY 50 ml OF LIQUID}}$$

FIGURE 16. GEOMETRICAL CORRECTION
FACTOR FOR LIQUID VOLUME

FIGURE 17. RATE OF DECREASE OF CHLORINE
CONCENTRATION FOR UNIRRADIATED ("DARK") RUN

9.3. Experimental Results

The experimental and calculated results for Experiments K-8 through K-16 are shown in Table XI and Figure 18. The results of Experiments K-2 through K-7 were discarded, when it became apparent that rather poor duplicability was caused by unsatisfactory removal of oxygen from the liquid.

Two methods were used for the calculation of reaction rates. The method of finite intervals will be illustrated for the first interval of Experiment K-8 (Table XI).

The concentrations of Cl_2 at the beginning and the end of the interval are obtained from the absorbance readings at $4000 \text{ \AA}$ (0.154 and 0.093) and converted to moles/liter with the aid of the calibration curve (Figure 9), giving respectively 27.2 and 16.4 mmol Cl_2 /l. From these values one obtains the average Cl_2 concentration during the interval (21.8 mmol/l) and the gross decrease in Cl_2 concentration (10.8 mmol/l). The "dark reaction" rate, obtained from Figure 17, multiplied by the time elapsed between samplings gives the change in (Cl_2) not due to irradiation (1.3 mmol/l). This value subtracted from the gross decrease in (Cl_2) gives the change in (Cl_2) due to irradiation (9.5 mmol/l). The apparent reaction rate of 9.5 mmol/(l)(min) is obtained by dividing the net change of (Cl_2) by the irradiation time of 1 min. For the liquid volume of 43 ml, the "Volume Dose Factor" obtained from Figure 16 is 1.05. The measured dose rate for a 50-ml volume multiplied by this factor gives the corrected dose rate for this interval, $1.05 \times 56.4 = 59.2 \text{ rad (solution)/min}$. Because of the radio-

FIGURE 18. SULFOCHLORINATION OF CYCLOHEXANE IN CARBON TETRACHLORIDE

active decay of fission products in the nuclear fuel elements, the radiation intensity decreases with time. In addition, variations in the gamma flux were caused by the movement of neighboring fuel elements. For the correlation of experimental data, it was desirable to refer reaction rates for a constant gamma intensity. This was done by multiplying the apparent reaction rate, calculated as shown above, by the square root of the ratio of the reference dose rate over the actual absorbed dose rate (in this case $\sqrt{56.4/59.2}$) to give the corrected reaction rate of 9.3 mmoles/(l)(min). The reaction velocity constant K was calculated from the empirical rate equation:

$$K = \frac{-\Delta (Cl_2)}{\Delta t} \bigg/ \sqrt{I (Cl_2) (C_{6H_{12}})} = 9.3 \bigg/ \sqrt{(56.4)(0.0218)(0.25)} \\ = 16.7 \times 10^{-3} \quad (1)$$

To obtain the actual amount of energy absorbed by the irradiated solution, one multiplies the experimentally determined gamma dose rate in water by an "Absorption Dose Factor;" in the illustrated case $41.5 \text{ rad (H}_2\text{O)/min} \times 1.360 = 56.4 \text{ rad (solution)/min}$. The Absorption Dose Factor varies with the composition of the solution, and several calculated values are shown in Table IX.

The correlation of the reaction rates with the several variables was done as follows:

(Cl₂) - The reaction rates obtained from Experiments K-8, 9, 10, 11, 12, 13 and 14 were plotted on logarithmic paper against (Cl₂), resulting in fairly straight and parallel lines with slopes close to 0.5 (Figures 19 and 21). This indicates that the rate varies as the square root of the Cl₂ concentration.

- (SO₂) - Experiments K-8 and 13 were performed under identical conditions, except for the SO₂ concentration, which was doubled in K-13. The results (Figure 19) show the reaction rate to be independent of SO₂ concentration.
- (C₆H₁₂) - In Experiments K-8, 9, 11 and 12, the only variable changed was the concentration of C₆H₁₂. The results are plotted in Figure 19. Figure 20 is a cross-plot, also on logarithmic coordinates, of four rate values taken from Figure 19 for a Cl₂ concentration of 0.015 mole/l. The slope of this line is 0.51, which indicates that the reaction rate is proportional to the square root of the concentration of C₆H₁₂.
- Gamma-
Radiation
Intensity
(I) - In Experiments K-8, 10, and 14, the only variable changed was the radiation intensity I. Results are plotted in Figure 21. Three values taken from each of these curves for (Cl₂) = 0.015 mole/l are cross-plotted in Figure 22. A straight line with a slope of 0.54 fits the plotted points quite well; therefore, the reaction rate also varies with the square root of the absorbed energy.

The results of this correlation are expressed by the following empirical equation:

$$-\frac{\Delta(\text{Cl}_2)}{\Delta t} = 1.08 \frac{\Delta(\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl})}{\Delta t} = K \sqrt{I (\text{Cl}_2)(\text{C}_6\text{H}_{12})} \quad (2)$$

The average of all calculated reaction velocity constants at 25°C is

$$K_{25} = 0.0154 \pm 0.000666 (\text{min})^{-1}(\text{rad})^{-0.5}.$$

FIGURE 19. EFFECT OF CHLORINE AND CYCLOHEXANE CONCENTRATIONS ON SULFOCHLORINATION RATE

FIGURE 20. EFFECT OF CYCLOHEXANE CONCENTRATION ON SULFOCHLORINATION RATE

FIGURE 21. EFFECT OF CHLORINE CONCENTRATION AND GAMMA RADIATION INTENSITY ON SULFO-CHLORINATION RATE OF CYCLOHEXANE

FIGURE 22. EFFECT OF GAMMA RADIATION INTENSITY ON SULFOCHLORINATION RATE OF CYCLOHEXANE

The indicated limits are for the 95% confidence level, the standard deviation being ± 0.00139 .

The two values for K_{35} (25.4 and 17.5×10^{-3}) do not agree too well, this being in part due to the uncertainty in determining the "dark reaction" rate at this temperature.

The results of Experiment K-16 show that the reaction is almost completely inhibited by oxygen.

In the alternate method of calculating reaction rates, the curves shown in Figure 18 were fitted by equations of the form

$$(\text{Cl}_2) = (-At + B)^n \quad (3)$$

where

$$(\text{Cl}_2) = \text{concentration of Cl}_2, \text{ mmoles/l}$$

$$t = \text{irradiation time, minutes}$$

$$A, B, n = \text{constants.}$$

The reaction rate is obtained by the differentiation of equation (3):

$$-\frac{d(\text{Cl}_2)}{dt} = An (-At + B)^{n-1} \quad (4)$$

$$\text{Since } (-At + B)^{n-1} = (\text{Cl}_2)^{\frac{n-1}{n}}, \quad (5)$$

one obtains by substitution in equation (4) an expression for the reaction rate as a function of chlorine concentration

$$-\frac{d(\text{Cl}_2)}{dt} = An (\text{Cl}_2)^{\frac{n-1}{n}} \frac{\text{mmoles}}{(\text{l})(\text{min})} \quad (6)$$

The values of the constants for all runs at 25°C and the derived rate equations are shown in the following table:

Run No.	A	B	n	$-\frac{d(Cl_2)}{dt}$
8	1.00	5.21	2.0	2.00 $(Cl_2)^{0.50}$
9	1.63	5.27	2.0	3.26 $(Cl_2)^{0.50}$
10	0.31	5.08	2.0	0.62 $(Cl_2)^{0.50}$
11	0.78	3.90	2.4	1.87 $(Cl_2)^{0.58}$
12	1.39	4.06	2.3	3.20 $(Cl_2)^{0.56}$
13	1.15	5.71	1.9	2.19 $(Cl_2)^{0.47}$
14	0.45	4.41	2.2	0.99 $(Cl_2)^{0.54}$

Chlorine concentrations calculated from equation (3) and the derived constants shown in the preceding table had an average deviation from the experimental values of -0.25% and only 3 out of 27 points deviated by over 5%.

The average value of the (Cl_2) exponent in the rate equation is 0.52.

The effect of (C_6H_{12}) concentration on the reaction rate is obtained for one Cl_2 concentration (15 mmols/l) in equation (6), using the derived constants for A, B and n. Results are shown below:

(C_6H_{12}) , mole/l	Rate, * $\frac{\text{mmoles } Cl_2}{(l) (min)}$
0.250	7.74
0.500	8.99
0.750	12.60
1.000	14.55

* not corrected for variations in radiation intensity.

These calculated points coincide with those shown in Figure 20, which were obtained by interpolation from Figure 19. The slope of the curve in Figure 20 is 0.51.

The effect of gamma intensity was calculated in a similar manner.

Results are shown below for $(\text{Cl}_2) = 15 \text{ mmol/l}$:

Gamma Intensity, rad (solution)/min	Rates, $\frac{\text{mmol Cl}_2}{(\text{l}) (\text{min})}$
6.79	2.40
26.5	4.40
56.4	7.75

Again, these calculated values are very close to those shown in Figure 22, which were obtained by interpolation from Figure 21. The slope of the curve in Figure 22 is 0.54.

By combining these results, one obtains the following empirical equation:

$$-\frac{d(\text{Cl}_2)}{dt} = 1.08 \frac{d(\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl})}{dt} = K I^{0.54} (\text{C}_6\text{H}_{12})^{0.51} (\text{Cl}_2)^{0.52} \quad (7)$$

This simplifies to:

$$-\frac{d(\text{Cl}_2)}{dt} = 1.08 \frac{d(\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl})}{dt} = K \sqrt{I (\text{C}_6\text{H}_{12}) (\text{Cl}_2)} \quad , \quad (8)$$

which is the same empirical equation obtained using the finite increment method of calculation.

9.4. Discussion of Results

The great rapidity with which the sulfochlorination of cyclohexane in carbon tetrachloride was found to proceed when initiated by gamma radiation immediately suggested a chemical chain reaction of considerable chain length. Such a chain reaction has been previously postulated for the photochemical sulfochlorination of aliphatic and cycloaliphatic hydrocarbons. The strong inhibiting action of oxygen is an indication of the free radical mechanism of this reaction.

Kharasch and co-workers⁽⁴⁶⁾ proposed the following mechanism for the photochemical sulfochlorination of aliphatic hydrocarbons:

The following calculated reaction rate is obtained from this scheme:

$$-\frac{d(\text{Cl}_2)}{dt} = k_2 \sqrt{\frac{2I_{\text{abs}}}{k_5}} (\text{RH}), \quad (6)$$

where I_{abs} is the absorbed light energy.

Indeed, Stauff⁽⁷⁶⁾ has found that the photochemical sulfochlorination of heptane and hexadecane in CCl_4 conforms to the following empirical rate equation:

$$-\frac{\Delta \text{Cl}_2}{\Delta t} = K \sqrt{I_{\text{abs}}} (\text{RH}). \quad (7)$$

The rate equation derived in the present investigation for the gamma-induced sulfochlorination differs from the above. This is not surprising if one considers that the photochemical reaction must be initiated by the dissociation of a Cl_2 molecule, since in the range of the spectrum in which the reaction was carried out ($4360 \text{ \AA}$) Cl_2 is the only component with a strong absorption band.

The interaction of gamma radiation with matter leads to the production of excited molecules or atoms, which are capable of initiating chemical reactions in a manner generally associated with free radicals.

In the present system, the concentrations of Cl_2 and SO_2 were quite low, making it unlikely that any appreciable number of primary initiating free radicals originate from these components. Both C_6H_{12} and CCl_4 are known to produce free radicals under gamma irradiation.⁽⁹⁾ The number of free radicals formed were estimated by scavenging them with diphenylpicrylhydrazyl or by initiating the polymerization of styrene and determining the number of polymer chains thus formed. These results indicate that the number of free radicals produced by irradiating CCl_4 is at least three times the number of free radicals from the radiolysis of C_6H_{12} . Other investigators⁽⁸⁹⁾ have measured the free Cl_2 produced during the irradiation of pure CCl_4 . They have postulated that the formation of Cl_2 proceeds by the following mechanism:

The numerical results from both studies will be used in calculating the average chain length of the gamma-induced sulfochlorination of cyclohexane. If one further considers that there were 10 to 40 times as many CCl_4 than there were C_6H_{12} molecules in the irradiated solution, it follows that the number of free radicals produced by the radiolysis of CCl_4 exceeds by far those originating from the radiolysis of C_6H_{12} . Consequently, in the proposed reaction mechanism it will be assumed that the chain reaction is initiated by free radicals from CCl_4 . The excellent agreement between the reaction rate equation derived from the proposed mechanism scheme and that arrived at by correlating the experimental data is an indirect proof for the correctness of the postulated mechanism.

9.4.1. The Mechanism of the Direct Sulfochlorination of Cyclohexane in Carbon Tetrachloride

Over-all reaction: $C_6H_{12} + SO_2 + Cl_2 = C_6H_{11}SO_2Cl + HCl$

Rate equation derived from experimental data:

$$-\frac{d(Cl_2)}{dt} = K \sqrt{I (Cl_2) (C_6H_{12})}$$

Proposed mechanism:

$$-\frac{d(Cl_2)}{dt} = k_4 (C_6H_{11}SO_2\cdot) (Cl_2) \quad (6)$$

$$\begin{aligned} \frac{d(C_6H_{11}SO_2\cdot)}{dt} &= k_3 (C_6H_{11}\cdot) (SO_2) - k_4 (C_6H_{11}SO_2\cdot) (Cl_2) \\ &\quad - k_5 (C_6H_{11}SO_2\cdot) (Cl\cdot) \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{d(Cl\cdot)}{dt} &= 2 I - k_2 (C_6H_{12}) (Cl\cdot) + k_4 (C_6H_{11}SO_2\cdot) (Cl_2) \\ &\quad - k_5 (C_6H_{11}SO_2\cdot) (Cl\cdot) \end{aligned} \quad (8)$$

[In (8) the rate of formation of $Cl\cdot$ also includes the formation of $CCl_3\cdot$.]

$$\frac{d(C_6H_{11}\cdot)}{dt} = k_2 (C_6H_{12}) (Cl\cdot) - k_3 (C_6H_{11}\cdot) (SO_2) \quad (9)$$

For steady state conditions, the rates given by equations (7), (8), and (9) are all zero.

Then from the addition of Equations (7), (8) and (9) there is obtained:

$$I = k_5(C_6H_{11}SO_2^{\cdot})(Cl^{\cdot}) \text{ or } (C_6H_{11}SO_2^{\cdot}) = \frac{I}{k_5(Cl^{\cdot})} \quad (10)$$

By adding Equations (7) and (9):

$$-k_4(C_6H_{11}SO_2^{\cdot})(Cl_2) - k_5(C_6H_{11}SO_2^{\cdot})(Cl^{\cdot}) + k_2(C_6H_{12})(Cl^{\cdot}) = 0 \quad (11)$$

By substituting Equation (10) for $(C_6H_{11}SO_2^{\cdot})$:

$$\frac{-k_4 I(Cl_2)}{k_5(Cl^{\cdot})} - \frac{k_5 I(Cl^{\cdot})}{k_5(Cl^{\cdot})} + k_2(C_6H_{12})(Cl^{\cdot}) = 0 \quad (12)$$

$$k_2 k_5(C_6H_{12})(Cl^{\cdot})^2 - k_5 I(Cl^{\cdot}) - k_4 I(Cl_2) = 0 \quad (13)$$

By solving the quadratic equation (13) for $(Cl^{\cdot})$ there is obtained

$$(Cl^{\cdot}) = \frac{1}{(C_6H_{12}) k_2} \left\{ \frac{I}{2} \pm \sqrt{\frac{I^2}{4} + \frac{k_2 k_4 I(Cl_2)(C_6H_{12})}{k_5}} \right\} \quad (14)$$

In Equation (14) $\frac{I}{2}$ and $\frac{I^2}{4}$ are small compared with the other term under the square root and can thus be neglected:

$$(Cl^{\cdot}) = \frac{1}{k_2} \sqrt{\frac{k_2 k_4 I(Cl_2)}{k_5(C_6H_{12})}} \quad (15)$$

Replacing the calculated value for $(Cl^{\cdot})$ in Equation (10):

$$(C_6H_{11}SO_2^{\cdot}) = \frac{k_2 I}{k_5} \sqrt{\frac{k_5(C_6H_{12})}{k_2 k_4 I(Cl_2)}} = \sqrt{\frac{k_2 I(C_6H_{12})}{k_4 k_5 (Cl_2)}} \quad (16)$$

Substituting (16) in (6) there is obtained the equation for the disappearance rate of Cl_2 :

$$-\frac{d(\text{Cl}_2)}{dt} = k_4 \sqrt{\frac{k_2 I (\text{C}_6\text{H}_{12})}{k_4 k_5 (\text{Cl}_2)}} \quad (\text{Cl}_2) = \sqrt{\frac{k_2 k_4}{k_5}} I (\text{Cl}_2) (\text{C}_6\text{H}_{12}) \quad (17)$$

Equation (17) as derived from the proposed mechanism for the chain reaction is identical with the empirical equation if the equality

$$K = \sqrt{\frac{k_2 k_4}{k_5}} \quad (18)$$

is made.

9.4.2. Radiochemical Yields and Chain Lengths

The G-number for the consumption of Cl_2 is numerically equal to the G-number for the production of $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ multiplied by 1.08:

$$-G_{\text{Cl}_2} = 1.08 G_{\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}} \quad .$$

Experimental Conditions:

$$(\text{Cl}_2) = 0.015 \text{ mole/l}$$

$$(\text{C}_6\text{H}_{12}) = 0.250 \quad "$$

$$(\text{SO}_2) = 0.048 \quad "$$

$$I = 50 \text{ rad (solution)/min}$$

Density of solution: 1.56 g/cc at 25°

Reaction Rate (obtained from Figure 22):

$$\begin{aligned} -\frac{d(\text{Cl}_2)}{dt} &= 6.8 \times 10^{-3} \frac{\text{mole}}{(1)(\text{min})} = 6.8 \times 10^{-3} \times 6.02 \times 10^{23} \\ &= 4.09 \times 10^{21} \frac{\text{molecules}}{(1)(\text{min})} \end{aligned}$$

$$\begin{aligned} 1 \text{ rad (solution)} &= 100 \frac{\text{erg}}{\text{g}} \rightarrow 100 \frac{\text{erg}}{\text{g}} \times 1560 \frac{\text{g}}{\text{l}} \rightarrow 1.56 \times 10^5 \frac{\text{erg}}{\text{l}} \rightarrow \\ &\rightarrow 1.56 \times 10^5 \frac{\text{erg}}{\text{l}} \times 6.24 \times 10^{11} \frac{\text{ev}}{\text{erg}} \rightarrow 9.74 \times 10^{16} \frac{\text{ev}}{\text{l}} \end{aligned}$$

$$50 \frac{\text{rad}}{\text{min}} (\text{solution}) \rightarrow 50 \frac{\text{rad}}{\text{min}} \times 9.74 \times 10^{16} \frac{\text{ev/l}}{\text{rad}} =$$

$$= 4.87 \times 10^{18} \frac{\text{ev}}{(1)(\text{min})}$$

$$-G_{\text{Cl}_2} = 1.08 G_{\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}} = \frac{4.09 \times 10^{21} \text{ molecules}/(1)(\text{min}) \times 100}{4.87 \times 10^{18} \text{ ev}/(1)(\text{min})}$$

$$= 8.40 \times 10^4 \frac{\text{molecules}}{100 \text{ ev}}$$

For chemical engineering applications, it is desirable to express yields as lb of materials produced per kw-hour of absorbed gamma energy. Since 1 kw-hour equals 2.25×10^{25} ev and one lb of $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ contains $\frac{453 \times 6.02 \times 10^{23}}{182.5} = 1.495 \times 10^{24}$ molecules, the yield shown above converts to:

$$\frac{1}{1.08} \times \frac{8.40 \times 10^4}{10^2} \frac{\text{molecules}}{\text{ev}} \times 2.25 \times 10^{25} \frac{\text{ev}}{\text{kw-hour}}$$

$$\times \frac{10^{-24}}{1.495} \frac{\text{lb}}{\text{molecule}} = 1.18 \times 10^4 \frac{\text{lb}}{\text{kw-hour}}$$

It is interesting to note that, even though the concentrations for this yield calculation were taken arbitrarily and are obviously not optimum values, the yield of 1.18×10^4 lb/kw-hr ranks with some of the highest radiochemical yields reported to date as shown in the following table:

<u>Reaction</u>	<u>lb/kw-hour</u>	<u>Ref:</u>
$\text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_6\text{Cl}_6$	1×10^5	(33)
Polymerization of N-vinyl-pyrrollidone in water	2.2×10^4	(4)
Polymerization of acrylonitrile in water (with X rays)	5×10^5	(7)

The average chain length, n , expressed as molecules of product formed per initiating free radical, is obtained from the respective G numbers; thus:

$$n = \frac{G_{C_6H_{11}SO_2Cl}}{G_R} .$$

Since the two published values for the G_R of CCl_4 were obtained by different methods, the values differ somewhat. The G_R determined with DPPH⁽⁹⁾ is 18.4 while the G_R calculated from the amount of free chlorine generated by gamma irradiation⁽⁸⁹⁾ is 14.2.

$$n_1 = \frac{8.40 \times 10^4}{18.4} = 4.57 \times 10^3$$

$$\text{and } n_2 = \frac{8.40 \times 10^4}{14.2} = 5.91 \times 10^3.$$

$$\text{Thus } \bar{n} = 5.24 \times 10^3.$$

This value compares quite well with the quantum yield of 5×10^3 reported for the photochemical sulfochlorination of hydrocarbons.⁽²³⁾

Stauff⁽⁷⁶⁾ reported a quantum yield for the photochemical sulfochlorination of heptane of 3.5×10^4 for the following concentrations:

$$(C_7H_{14}) - 0.5 \text{ mole/l}$$

$$(Cl_2) - 0.05 \text{ "}$$

$$(SO_2) - 0.05 \text{ "}$$

If the chain length determined in this study is recalculated for the above concentrations with the aid of the empirical rate equation, there is obtained a value for n of 1.34×10^4 , which is of the same order of magnitude as the photochemical quantum yield.

This would support the assumption that, except for the initiation and termination steps, the mechanism of the gamma-induced chain reaction is similar to that of the photochemical sulfochlorination.

9.4.3. Thermodynamic Data

Activation energies can be estimated from the Arrhenius Equation:

$$K = A \exp (-E_a/RT),$$

where K = reaction velocity constant

A = frequency factor (characteristic for the particular system, and can be considered constant over a narrow temperature range)

E_a = apparent energy of activation.

From values for the reaction velocity constant at two temperatures, (in this case 25 and 35°C), E_a is obtained as follows:

$$\frac{K_{35}}{K_{25}} = \frac{A \exp (-E_a/RT_{35})}{A \exp (-E_a/RT_{25})} ,$$

and

$$E_a = \log (K_{35}/K_{25}) / \left(\frac{1}{RT_{25}} - \frac{1}{RT_{35}} \right) \log e.$$

The value for K_{25} was obtained from 20 rate determinations, and the average of 0.0154 has limits of only 4.3% for a 95% confidence level. The two values for K_{35} , however, do not agree as well and two separate calculations will be made for E_a .

For $K_{25} = 0.0154$ and $K_{35} = 0.0254$,

$$E_a = 9.1 \text{ kcal/g-mole.}$$

For $K_{25} = 0.0154$ and $K_{35} = 0.0175$,

$$E_a = 2.3 \text{ kcal/g-mole.}$$

Then $\overline{E_a} = 5.7 \text{ kcal/g-mole.}$

This compares very favorably with the value of 6.0 kcal/g-mole reported by Stauff for the photochemical sulfochlorination of heptane. From the rate equation derived from the proposed mechanism, it follows that

$$\frac{1}{2} (q_2 + q_4 - q_5) = 5.7,$$

where q_2 , q_4 and q_5 are respectively the activation energies for reactions 2, 4 and 5.

q_5 is probably quite small (reaction of two radicals).

q_2 has been estimated for the corresponding step in the reaction of n-heptane to be 6 kcal. Since this is unlikely to differ for cyclohexane one can also consider q_2 for this case to be equal to 6 kcal.

q_4 is then calculated to be 5.4 kcal. This high value is quite possible if one considers the fact that reaction (4), which accounts for the consumption of Cl_2 , is so strongly inhibited by O_2 . This is further supported by the activation energy of 9 kcal which has been calculated for the reaction

This reaction resembles reaction (4) in that it is also between a free radical and a chlorine molecule.

10. Conclusions

Gamma radiation cannot be used to accomplish the introduction of the $\text{-SO}_2\text{Cl}$ group into the benzene ring. Only chlorination by addition was found to occur, even for an excess of SO_2 . Nitrobenzene does not react with either SO_2Cl_2 or SO_2/Cl_2 mixtures in the presence of gamma radiation.

The direct sulfochlorination was successfully carried out with cyclohexane, the product consisting mainly of $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ and, to a smaller extent, $\text{C}_6\text{H}_{11}\text{Cl}$ and $\text{C}_6\text{H}_{10}(\text{SO}_2\text{Cl})_2$. Conversion rates were very high, and for SO_2/Cl_2 ratios greater than unity sulfochlorination exceeded chlorination by a factor of over twenty. For the experimental conditions of the present study, the rate of conversion to $\text{C}_6\text{H}_{11}\text{SO}_2\text{Cl}$ was proportional to the square root of the absorbed radiation dose, up to a dose rate of 40 rad/min. Above 400 rad/min, the conversion rate remained independent of dose rate at a constant value of $0.025 \frac{\text{g-mole}}{(\text{l})(\text{min})}$.

The sulfochlorination of aliphatic or cycloaliphatic hydrocarbons induced by gamma radiation may become commercially attractive, particularly in view of the expected lowering in the cost of radiation sources.

The results of the kinetics study of the sulfochlorination of cyclohexane in dilute carbon tetrachloride solutions showed this to be a chemical chain reaction with an approximate chain length of 5000. This reaction was very strongly inhibited by oxygen, suggesting a free radical mechanism. The empirical rate equation showed the rate to be proportional to the square root of the product of radiation intensity and Cl_2 and C_6H_{12} concentrations, but independent of SO_2 concentration, as long as this reactant was present in excess of the stoichiometric ratio.

The equation for the reaction rate derived from the proposed mechanism of the reaction was in excellent agreement with the experimental results.

The results of this study have added evidence to the hope that the radiation energy emanating from the fission products of uranium or other fissionable materials can be used advantageously for the initiation of certain chemical reactions.

11. Appendix

Experimental and Calculated Data

Bibliography

TABLE VIII
EXPERIMENTAL RESULTS - SULFOCHLORINATION OF CYCLOHEXANE

	Reaction Time: 90 min				C ₆ H ₁₂ Volume: 20 cc				Feed Gas Rate: 2.3 l/hr						
Run No.	46	47	48	50	51*	52	53	54	55	56	57	61	62	63	64
Date - 1957	10-28	10-28	10-29	10-31	10-31	11-8	11-8	11-11	11-11	11-12	11-12	12-4	12-5	12-5	12-6
SO ₂ /Cl ₂ (nominal) mole/mole	2	2	2	2	2	1	1	1	0.5	0.5	0.5	1	1	1	0.5
Reactor Temp, °C	11.5	11.6	11.6	25.0	40.0	11.5	25.0	40.0	25.0	11.5	40.0	25.0	11.5	40.0	40.0
Dose Rate, rad(H ₂ O)/min	0	7,300	7,200	7,200	7,100	6,300	6,300	6,100	6,100	6,000	6,000	86	85	85	83
Dose rate, rad(C ₆ H ₁₂)/min	0	5,830	5,750	5,750	5,670	5,030	5,030	4,870	4,870	4,790	4,790	69	68	68	66
Room Temp at Start, °C	22.0	22.0	22.0	23.0	23.0	20.0	20.0	23.0	23.0	20.5	23.0	21.0	21.9	21.8	21.0
Room Temp at End, °C	22.5	22.0	21.5	23.0	23.5	21.0	20.0	22.8	23.5	23.0	22.7	22.1	22.2	22.0	21.1
SO ₂ - initial pressure, psig	31.0	34.5	34.0	33.5	35.5	29.0	30.8	33.0	36.0	32.0	34.0	30.6	31.0	32.7	33.0
SO ₂ - final pressure, psig	9.8	13.4	12.7	12.2	13.0	12.8	14.8	16.8	25.1	21.0	23.1	14.2	14.6	16.2	22.1
SO ₂ - Wt initial, g	12.5	13.4	13.2	13.1	13.6	12.1	12.6	13.1	13.8	12.9	13.4	12.5	12.5	13.0	13.1
SO ₂ - Wt final, g	6.7	7.4	7.3	7.1	7.3	7.6	8.2	8.6	11.0	9.8	10.4	7.9	8.0	8.4	10.1
SO ₂ - ΔWt, g	5.8	6.0	5.9	6.0	6.3	4.5	4.4	4.5	2.8	3.1	3.0	4.6	4.5	4.6	3.0
SO ₂ - moles x 10 ³	90.6	93.6	92.1	93.6	98.3	70.2	68.7	70.2	43.7	48.4	46.8	71.8	70.2	71.8	46.8
Cl ₂ - initial pressure, psig	38.1	42.5	38.0	39.5	40.5	38.0	39.8	40.0	39.0	38.0	39.0	38.7	40.0	39.9	38.7
Cl ₂ - final pressure, psig	31.7	35.9	31.5	33.0	33.3	28.1	29.9	30.3	26.0	24.9	26.0	29.0	30.2	30.2	25.5
Cl ₂ - Wt initial, g	27.5	28.8	26.6	27.3	27.8	27.5	28.5	28.3	27.8	27.5	27.8	27.8	28.4	28.4	27.8
Cl ₂ - Wt final, g	24.2	25.5	23.3	24.0	24.2	22.5	23.4	23.4	21.3	20.7	21.3	22.8	23.4	23.4	21.1
Cl ₂ - ΔWt, g	3.3	3.3	3.3	3.3	3.6	5.0	5.1	4.9	6.5	6.8	6.5	5.0	5.0	5.0	6.7
Cl ₂ - moles x 10 ³	46.5	46.5	46.5	46.5	50.8	70.5	71.9	69.1	91.6	95.9	91.6	70.5	70.5	70.5	94.5
SO ₂ /Cl ₂ (actual) mole/mole	1.95	2.01	1.98	2.01	1.93	0.99	0.96	1.02	0.48	0.50	0.51	1.02	1.00	1.02	0.49
Total Product, Wt, g	0.01	8.04	9.50	7.51	9.63	11.52	12.91	8.53	11.37	14.88	15.78	3.38	7.89	4.14	9.84
Cl-Total(anal), %	-	17.43	17.20	18.33	17.75	18.63	18.85	18.11	22.51	25.81	23.84	20.37	15.11	19.33	23.63
Cl-Hydrolyzable(anal), %	-	17.22	17.50	17.74	17.41	16.67	15.73	15.49	12.94	11.25	10.12	14.38	10.79	13.13	7.99
Cl-Non-hydrolyzable, %	-	0.21	0.0	0.59	0.34	1.96	3.12	2.62	9.57	14.56	13.72	5.99	4.32	6.20	15.64
S (anal), %	-	15.50	15.47	16.04	-	-	-	-	-	10.15	-	-	-	-	7.21
Cl _H .h/Cl _H	-	0.01	0.0	0.03	0.02	0.12	0.20	0.17	0.74	1.30	1.36	0.42	0.40	0.47	1.96
Conversion to RSO ₂ , Cl, %	0	83.9	100.0	80.7	93.1	77.0	83.5	53.9	95.0	97.5	96.0	19.4	34.0	21.7	47.2
Conversion based on	-	Cl ₂	Cl ₂	Cl ₂	Cl ₂	SO ₂	SO ₂	Cl ₂	SO ₂	SO ₂	SO ₂	Cl ₂	Cl ₂	Cl ₂	SO ₂
C RSO ₂ Cl x 10 ⁻³	0	4.6	5.7	4.5	5.3	7.5	7.9	5.3	5.9	6.8	6.5	138	250	157	230
n, Chain length, x 10 ⁻³	-	0.52	0.65	0.51	0.60	0.85	0.90	0.60	0.67	0.77	0.74	15.7	28.4	17.8	26.2

* Duration of Run 98 min

TABLE VIII
EXPERIMENTAL RESULTS (Continued) - SULFOCHLORINATION OF CYCLOHEXANE

Run No.	65	66	67	68	69	70	71	73	74	75	76	77	78	79	80	81	82	83	84
Date - 1957/58	12-6	12-9	12-9	12-10	12-10	12-11	12-13	12-17	12-17	12-26	12-26	12-27	12-27	12-30	12-30	12-31	2-10	2-14	2-19
SO ₂ /Cl ₂ (nominal) mole/mole	0.5	0.5	2	2	2	1	1	1	1	1	2	2	2	0.5	0.5	0.5	2	2	2
Reactor Temp, °C	11.5	25.0	11.5	25.0	40.0	11.5	11.5	11.5	25.0	40.0	25.0	11.5	40.0	25.0	11.5	40.0	11.5	11.5	11.5
Dose Rate, rad(H ₂ O)/min	83	80	80	79	79	0	628	583	583	531	531	528	528	518	518	515	41.4	4.97	19.4
Dose Rate, rad(C ₆ H ₁₂)/min	66	64	64	63	63	0	501	466	466	424	424	422	422	414	414	411	34.0	3.97	15.5
Room Temp Start, °C	21.1	19.6	22.5	21.0	22.1	18.4	20.6	21.3	23.1	22.0	22.5	22.3	20.6	20.6	21.8	22.0	19.0	21.0	20.6
Room Temp End, °C	21.5	21.2	22.2	20.5	22.6	19.0	22.1	23.1	22.3	22.6	22.8	22.0	23.1	24.1	22.0	22.5	18.5	22.0	21.0
SO ₂ - initial pressure, psig	32.4	31.9	32.2	31.7	31.2	25.9	29.0	31.8	33.0	31.0	33.4	31.0	32.0	31.1	33.4	32.6	30.0	31.2	31.0
SO ₂ - final pressure, psig	21.4	21.0	10.0	9.9	9.5	9.5	12.5	15.4	16.6	14.7	11.4	9.1	10.1	20.3	22.5	21.8	8.2	9.4	9.2
SO ₂ - Wt initial, g	13.0	13.0	12.9	12.8	12.8	11.4	12.0	12.8	13.1	12.5	13.2	12.5	12.9	12.6	13.2	13.0	12.4	12.6	12.5
SO ₂ - Wt final, g	9.9	9.8	6.8	6.8	6.7	6.8	7.5	8.2	8.6	8.1	7.2	6.6	6.8	9.6	10.2	10.0	6.4	6.6	6.6
SO ₂ - ΔWt, g	3.1	3.2	6.1	6.0	6.1	4.6	4.5	4.6	4.5	4.4	6.0	5.9	6.1	3.0	3.0	3.0	6.0	6.0	5.9
SO ₂ , moles x 10 ³	48.4	49.9	95.2	93.6	95.2	71.8	70.2	71.8	70.2	68.7	93.6	92.1	95.2	46.8	46.8	46.8	93.6	93.6	92.3
Cl ₂ initial pressure, psig	38.6	40.0	39.8	40.0	40.0	40.0	39.1	39.9	40.0	39.8	40.0	40.0	39.8	40.0	40.0	40.0	40.0	40.0	39.9
Cl ₂ final pressure, psig	25.4	27.0	33.0	33.2	33.2	30.2	29.4	30.1	30.2	30.0	33.1	33.3	33.1	27.0	27.0	27.0	33.2	33.2	33.1
Cl ₂ - Wt initial, g	27.7	28.7	28.2	28.5	28.3	28.8	28.0	28.4	28.3	28.3	28.3	28.3	28.4	28.5	28.4	28.4	28.5	28.4	28.5
Cl ₂ - Wt final, g	21.0	21.8	24.8	25.1	24.8	23.7	23.0	23.3	23.3	23.3	24.8	24.9	24.8	21.7	21.8	21.8	25.2	24.9	24.9
Cl ₂ - ΔWt, g	6.7	6.9	3.4	3.4	3.5	5.1	5.0	5.1	5.0	5.0	5.5	3.4	3.6	6.8	6.6	6.6	3.3	3.5	3.6
Cl ₂ , Moles x 10 ³	94.5	97.3	47.9	47.9	49.3	71.9	70.5	71.9	70.5	70.5	49.3	49.9	50.8	95.9	93.1	93.1	46.5	49.4	50.8
SO ₂ /Cl ₂ (actual) mole/mole	0.51	0.51	1.99	1.95	1.95	1.93	1.00	1.00	1.00	0.97	1.90	1.92	1.87	0.49	0.50	0.50	2.01	1.90	1.82
Total Product Wt, g	10.81	7.58	8.67	8.43	8.71	0.02	11.04	12.43	11.36	10.94	8.80	9.36	9.05	13.63	13.69	12.16	7.20	2.83	5.70
Cl-Total (anal), %	25.36	26.10	19.12	18.63	17.11	-	18.09	17.65	18.55	18.46	17.99	17.68	18.18	18.42	18.78	21.82	-	-	-
Cl-Hydrolyzable (anal), %	8.42	8.23	16.86	16.33	14.09	-	15.17	16.21	16.01	14.83	17.76	17.46	17.90	7.79	9.74	9.92	16.73	15.64	16.23
Cl-Non-hydrolyzable, %	16.94	17.87	2.26	2.30	3.02	-	2.92	1.44	2.54	3.63	0.23	0.22	0.28	10.63	9.04	11.90	-	-	-
S (anal), %	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cl _{N.H} /Cl _H	2.01	2.17	0.13	0.14	0.21	-	0.19	0.09	0.16	0.24	0.01	0.01	0.02	1.36	0.93	1.20	-	-	-
Conversion to RSO ₂ Cl, %	53.1	35.2	86.0	81.0	70.1	0.0	67.0	79.0	72.7	66.6	89.3	92.4	90.0	64.0	80.2	72.7	73.1	25.2	51.3
Conversion based on	SO ₂	SO ₂	Cl ₂	Cl ₂	Cl ₂	-	Cl ₂	Cl ₂	Cl ₂	SO ₂	Cl ₂	Cl ₂	Cl ₂	SO ₂	SO ₂	SO ₂	Cl ₂	Cl ₂	Cl ₂
G RSO ₂ Cl x 10 ⁻³	270	191	450	430	380	0	66	85	77	75	72	76	75	50	63	57	695	2185	1170
n, Chain length, x 10 ⁻³	30.7	21.7	51.1	48.9	43.2	-	7.50	9.66	8.75	8.53	8.19	8.64	8.53	5.68	7.16	6.48	79.0	248.5	133.0

Table IX

Calculated Absorption Dose Factors for Mixtures ofC₆H₁₂ and CCl₄

(C ₆ H ₁₂), $\frac{\text{mole}}{\text{l}}$	Density of Solution, $\frac{\text{g}}{\text{cc}}$ at 25°C	(CCl ₄), $\frac{\text{mole}}{\text{l}}$	<u>No. of Electrons per cc of Solution</u>			Absorption Dose Factor (1)
			(C ₆ H ₁₂) $\times 10^{-23}$	CCl ₄ $\times 10^{-23}$	Total $\times 10^{-23}$	
0.250	1.56	10.00	0.072	4.450	4.522	1.360
0.500	1.54	9.75	0.144	4.340	4.484	1.345
0.750	1.52	9.48	0.217	4.220	4.437	1.330
1.000	1.50	9.22	0.289	4.110	4.399	1.318

$$(1) \text{ Absorption Dose Factor} = \frac{\text{Absorption Coefficient of Solution}}{\text{Absorption Coefficient of Water}} = \frac{\text{No. of Electrons per cc of Soln}}{\text{No. of Electrons per cc of Water}}$$

$$\text{No. of Electrons per cc of Water} = 3.33 \times 10^{23}$$

Table X

Experiment No. K - 1Rate of Decrease of Chlorine Concentration forUnirradiated ("Dark") Run

Time from Start of Gas Introduction,	Δt ,	(Cl_2) ,	(Cl_2) ,	ΔCl_2 ,	$(Cl_2)_{ave}$,	$\frac{\Delta Cl_2}{\Delta t}$,
min	min	absorbance	$\frac{\text{mole}}{l}$ $\times 10^3$	$\frac{\text{mole}}{l}$ $\times 10^3$	$\frac{\text{mole}}{l}$ $\times 10^3$	$\frac{\text{mole}}{(l)(min)}$ $\times 10^3$
31.00		0.144	25.4			
	16.00			2.1	24.3	0.13
47.00		0.132	23.3			
	15.50			1.0	22.8	0.065
62.50		0.126	22.3			
	29.30			1.1	21.7	0.038
91.80		0.120	21.2			

Temperature: 25°CConcentrations in mole/liter: C_6H_{12} - 0.250; Cl_2 - 0.026; SO_2 - 0.058.

Table XI

EXPERIMENT No. K - 8

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
Time, (1)	Operation, (2)	Δt_S , (3)	Δt_I , (4)	(Cl_2) , Absorbance	(Cl_2) , $\frac{\text{mole}}{l}$	$(Cl_2)_{ave}$, $\frac{\text{mole}}{l}$	$\Delta(Cl_2)_S$, $\frac{\text{mole}}{l}$	$\Delta(Cl_2)_D$, $\frac{\text{mole}}{l}$	$\Delta(Cl_2)_I$, $\frac{\text{mole}}{l}$	$\Delta(Cl_2)_I$, $\frac{\text{mole}}{(l)(\text{min})}$	Volume, ml	Volume Dose Factor,	Corr. Dose Rate,	$\frac{\Delta(Cl_2)}{\Delta t}$, $\frac{\text{mole}}{(l)(\text{min})}$	K, $\times 10^3$
min		min	min		$\times 10^3$	$\times 10^3$	$\times 10^3$	$\times 10^3$	$\times 10^3$	$\times 10^3$			$\frac{\text{rad}}{\text{min}}$ (soln)	$\times 10^3$	$\times 10^3$
35.50	S			0.154	27.2										
39.69	IS														
40.69	IT	10.00	1.00			21.8	10.8	1.3	9.5	9.5	43	1.05	59.2	9.3	16.7
45.50	S			0.093	16.4										
49.35	IS														
50.35	IT	8.00	1.00			12.7	7.4	-	7.4	7.4	39	1.07	60.4	7.2	17.0
53.50	S			0.051	9.0										
58.88	IS														
59.88	IT	10.05	1.00			6.5	5.3	-	5.5	5.3	35	1.08	60.9	5.1	16.9
63.55	S			0.021	3.7										

Temperature: 25 °C

Density of Solution: 1.56 g/cc

Absorption Dose Factor: 1.360

Gamma Intensity: 41.5 rad (H₂O)/min = 56.4 rad (solution)/min

Reference Dose Rate: 56.4 rad (solution)/min

Concentrations, in mole/liter: C₆H₁₂ = 0.250; Cl₂ initial = 0.028; SO₂ initial = 0.058.

- (1) Elapsed time from start of gas introduction. (2) S = sampled, IS = irradiation started, IT = irradiation terminated.
 (3) Time interval between samplings. (4) Irradiation time. (5) Total change in (Cl₂) during Δt_S . (6) Change in (Cl₂) due to "dark reaction." (7) Change in (Cl₂) due to irradiation.

Table XI

EXPERIMENT No. K - 9

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
29.30	S			0.158	27.8										
33.53	IS														
34.53	IT	10.35	1.00			19.8	15.9	1.3	14.6	14.6	43	1.05	54.8	14.8	16.1
39.65	S			0.067	11.9										
44.37	IS														
45.37	IT	9.40	1.00			7.4	9.1	-	9.1	9.1	39	1.07	55.8	9.2	16.4
49.05	S			0.016	2.8										

Temperature: 25°CDensity of Solution: 1.52 g/ccAbsorption Dose Factor: 1.330Gamma Intensity: 41.5 rad(H₂O)/min = 52.2 rad(solution)/min Reference Dose Rate: 56.4 rad(solution)/minConcentrations in mole/liter: C₆H₁₂ - 0.750; Cl₂ initial - 0.028; SO₂ initial - 0.058

Table XI

EXPERIMENT No. K - 10

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
35.00	S			0.146	25.8										
39.38	IS														
40.38	IT	9.30	1.00			23.8	3.9	1.1	2.8	2.80	43	1.05	7.14	2.73	13.6
44.30	S			0.124	21.9										
50.30	IS														
52.30	IT	12.70	2.00			19.0	5.7	0.1	5.6	2.80	39	1.07	7.26	2.70	15.0
57.00	S			0.092	16.2										
63.17	IS														
66.17	IT	12.00	3.00			12.5	7.5	-	7.5	2.50	35	1.08	7.34	2.40	16.4
69.00	S			0.049	8.7										
75.70	IS														
78.70	IT	14.00	3.00			6.4	4.6	-	4.6	1.53	31	1.08	7.34	1.47	14.2
83.00	S			0.023	4.1										

Temperature: 25°CDensity of Solution: 1.56 g/ccAbsorption Dose Factor: 1.360Gamma Intensity: 4.99 rad(H₂O)/min = 6.79 rad(solution)/minReference Dose Rate: 6.79 rad(solution)/minConcentrations in mole/liter: C₆H₁₂ - 0.250; Cl₂ initial - 0.027; SO₂ initial - 0.058

Table XI

EXPERIMENT No. K - 11

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
23.40	S			0.148	26.1										
32.20	IS														
33.20	IT	12.20	1.00			19.6	12.9	1.7	11.2	11.2	43	1.05	61.0	10.8	14.6
35.60	S			0.075	13.2										
42.20	IS														
43.20	IT	11.50	1.00			9.4	7.6	-	7.6	7.6	39	1.07	62.1	7.2	14.0
47.10	S			0.032	5.6										
53.41	IS														
54.41	IT	11.70	1.00			3.5	4.2	-	4.2	4.2	35	1.08	62.7	4.0	12.7
58.80	S			0.008	1.4										

Temperature: 25°CDensity of Solution: 1.54 g/ccAbsorption Dose Factor: 1.345Gamma Intensity: 43.1 rad(H₂O)/min = 58.0 rad(solution)/min Reference Dose Rate: 56.4 rad(solution)/minConcentrations in mole/liter: C₆H₁₂ - 0.500; Cl₂ initial - 0.027; SO₂ initial - 0.058.

Table XI

EXPERIMENT No. K - 12

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
28.00	S			0.143	25.2										
33.48	IS														
34.48	IT	10.00	1.00			16.6	17.2	1.3	15.9	15.9	43	1.05	59.7	15.5	16.0
38.00	S			0.045	8.0										
44.31	IS														
45.31	IT	9.60	1.00			4.3	7.5	-	7.5	7.5	39	1.07	60.8	7.2	14.7
47.60	S			0.003	0.5										

Temperature: 25°CDensity of Solution: 1.50 g/ccAbsorption Dose Factor: 1.318Gamma Intensity: 43.1 rad(H₂O)/min = 56.8 rad(solution)/min Reference Dose Rate: 56.4 rad(solution)/minConcentrations in mole/liter: C₆H₁₂ - 1.000; Cl₂ initial - 0.026; SO₂ initial - 0.058.

Table XI

EXPERIMENT No. K - 13

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
27.00	S			0.155	27.4										
32.40	IS														
33.40	IT	9.50	1.00			22.0	10.8	1.3	9.5	9.5	43	1.05	61.1	9.1	16.4
36.50	S			0.094	16.6										
41.47	IS														
42.47	IT	8.70	1.00			12.7	7.9	-	7.9	7.9	39	1.07	62.3	7.5	17.7
45.20	S			0.049	8.7										
51.37	IS														
52.37	IT	10.10	1.00			6.1	5.2	-	5.2	5.2	35	1.08	62.8	4.9	16.8
55.30	S			0.020	3.5										

Temperature: 25°CDensity of Solution: 1.50 g/ccAbsorption Dose Factor: 1.360Gamma Intensity: 42.8 rad(H₂O)/min = 58.2 rad (solution)/minReference Dose Rate: 56.4 rad(solution)/minConcentrations in mole/liter: C₆H₁₂ - 0.250; Cl₂ initial - 0.027; SO₂ initial - 0.116

Table XI

EXPERIMENT No. K - 14

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
28.30	S			0.148	26.2										
33.27	IS														
35.27	IT	10.20	2.00			20.3	11.9	1.3	10.6	5.30	43	1.05	27.9	5.16	14.1
38.50	S			0.081	14.3										
42.50	IS														
44.50	IT	9.55	2.00			10.3	7.9	-	7.9	3.95	39	1.07	28.4	3.81	14.6
48.05	S			0.036	6.4										
54.04	IS														
56.04	IT	10.45	2.00			4.1	4.5	-	4.5	2.25	35	1.08	28.6	2.16	13.1
58.50	S			0.011	1.9										

Temperature: 25°CDensity of Solution: 1.56 g/ccAbsorption Dose Factor: 1.360Gamma Intensity: 19.5 rad (H₂O)/min = 26.5 rad(solution)/minReference Dose Rate: 26.5 rad(solution)/minConcentrations in mole/liter: C₆H₁₂ - 0.250; Cl₂ initial - 0.027; SO₂ initial 0.058.

Table XI

EXPERIMENT No. K - 15

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
34.40	S			0.156	27.5										
41.49	IS														
42.49	IT	11.80	1.00			19.2	16.5	2.8	13.7	13.7	43	1.05	60.6	13.4	25.4
46.20	S			0.062	11.0										
52.15	IS														
53.15	IT	10.30	1.00			7.9	6.1	-	6.1	6.1	39	1.07	61.9	5.9	17.5
56.50	S			0.028	4.9										

Temperature: 35°CDensity of Solution: 1.56 g/ccAbsorption Dose Factor: 1.360Gamma Intensity: 42.5 rad(H₂O)/min = 57.8 rad(solution)/min Reference Dose Rate: 57.8 rad(solution)/minConcentrations in mole/liter: C₆H₁₂ - 0.250; Cl₂ initial - 0.028; SO₂ initial - 0.058.

Table XI

EXPERIMENT No. K - 16

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
28.00	S			0.163	28.8										
34.80	IS														
35.80	IT	11.60	1.00			28.1	1.4	1.3	0.1	0.1	43	1.05	60.6	0.096	
39.60	S			0.155	27.4										
47.83	IS														
57.83	IT	21.70	10.00			26.3	2.1	1.1	1.0	0.1	39	1.07	61.8	0.096	
61.30	S			0.143	25.3										

Temperature: 25°CDensity of Solution: 1.56 g/ccAbsorption Dose Factor: 1.360Gamma Intensity: 42.5 rad(H₂O)/min = 57.8 rad(solution)/minReference Dose Rate: 56.4 rad(solution)/minConcentrations in mole/liter: C₆H₁₂ - 0.250; Cl₂ initial - 0.029; SO₂ initial - 0.058.Solution was saturated with oxygen before irradiation

Table XII

Analytical Results for Material Balances

<u>Experiment No.</u>	<u>S - 1</u>	<u>S - 2</u>	<u>S - 3</u>	<u>S - 4</u>
Cl ₂ initial,	28.0	27.0	26.2	26.9
Cl ₂ final,	11.0	5.9	9.1	7.3
Cl ₂ difference,	17.0	21.1	17.1	19.6
Cl ₂ lost by "dark reaction,"	1.1	1.3	1.3	1.2
Cl ₂ reacted,	15.9	19.8	15.8	18.4
SO ₂ initial,	54.0	58.0	116.0	58.0
SO ₂ final,	38.0	38.0	99.0	39.0
SO ₂ reacted,*	16.0	20.0	17.0	19.0
C ₆ H ₁₂ initial,	250.0	750.0	250.0	250.0
HCl produced,	16.0	19.0	16.0	18.0
C ₆ H ₁₁ SO ₂ Cl produced,	15.0	18.0	15.0	17.0
C ₆ H ₁₁ SO ₂ Cl/ Δ Cl ₂	0.93	0.91	0.95	0.92

All concentrations are in mole/liter x 10³.

* The amount of SO₂ lost by "dark reaction" could not be determined.

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