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AECU-2888

CHLORINATION OF SOME AROMATIC COMPOUNDS UNDER THE
INFLUENCE OF GAMMA RADIATION

NO. 43868

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Introduction

The preceding paper discusses the effect of gamma radiation from cobalt-60 sources on the polymerization of ethylene. This paper presents data obtained when certain aromatic compounds have been treated with chlorine in a field of gamma rays.

The reaction of chlorine with aromatic compounds can occur in three ways: substitution for hydrogen on the ring, substitution for hydrogen in alkyl groups attached to the ring, and saturation of the aromatic ring by addition of three moles of halogen. Substitution on the ring is favored by halogen carriers, notably iron salts, iodine, or similar agents and in the presence of these materials, the reaction occurs at relatively low temperatures. In the case of benzene, ultra-violet light activates addition to the ring, but in an alkyl benzene such as toluene, it accelerates side chain substitution; the latter reaction usually requires elevated temperatures in order to take place at a reasonable speed. Alyea (1) showed that alpha radiation also promotes addition of chlorine to benzene.

Reaction of Benzene

When chlorine was bubbled through benzene in the presence of gamma radiation from a cobalt-60 source, a vigorous reaction took place. Analyses of the reaction mixture and of the tail

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gases showed that chlorine combined with the benzene by addition. When pure benzene was used, the reaction proceeded so rapidly that temperature control was difficult and the chlorine inlet line soon became plugged with solid product. Most of the experiments with benzene, therefore, were conducted in carbon tetrachloride solutions. In these runs, virtually complete reaction was realized in about twenty minutes.

The solid material isolated from the reaction between benzene and chlorine was analyzed and found to be a mixture of the stereoisomers of nearly-pure 1,2,3,4,5,6-hexachlorocyclohexane. An infra-red analysis* demonstrated that the mixture contains

*The authors are indebted to the E. I. duPont de Nemours and Company, Engineering Service Division, for the analyses for gamma isomer listed here.

about 12-13 per cent of the gamma isomer, a composition which corresponds with that of the product of commercial processes employing ultra violet radiation. Table I indicates the results of a few experiments in a 1 kilocurie cobalt-60 source.

(See Fig. 1)

TABLE I

ANALYSES OF SOME SAMPLES OF BENZENE HEXACHLORIDE

Approximate Temperature of Reaction, °C	% Benzene (by volume)	% CCl ₄ (solvent) (by volume)	% Gamma Isomer in Benzene Hexachloride (from infra-red analysis)
20	10	90	11.3 (over chlorinated)
20	20	80	12.5
-10	10	90	12.3
-10	30	70	12.8

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In order to compare this reaction with others in the field of radiation chemistry, an approximate value for "G" (molecules reacted per 100 e.v. of gamma energy absorbed by the system) was calculated. For this calculation, a typical reaction of chlorine and 20% benzene in carbon tetrachloride at 25°C. was chosen. Dose rates for gamma irradiation were based on measurements in air by the ferrous sulfate method (2), and the entire volume of the solution was considered in calculation of the dose absorbed. The value for G thus obtained was 85,000. This value indicates a long reaction chain length. Since it has been reported that 32.5 electron volts are required to produce an ionized atom (3), and if it is assumed that every primary ionization event produces one radical, a minimum chain length of 2.8×10^4 is indicated.

Reaction of Toluene

The reaction of chlorine with toluene has also been studied in a one kilocurie gamma source (See Fig. 1). A considerable amount of addition to the ring took place and there was a certain amount of substitution in the side chain in some of the material. Comparative runs in the absence of gamma irradiation gave only small amounts of chlorinated products.

A number of runs using toluene and chlorine have been made in the radiation field of a 10 kilo-curie cobalt-60 source. (See Fig. 2) For these runs, about 1.5 liters of toluene was placed in the reactor. The air in the system was displaced by nitrogen and the solution was saturated with chlorine before the cobalt source was raised out of its storage well at the start of the reaction. During the entire period of chlorination, to minimize photochlorination, only red light was used whenever it was necessary to observe the equipment. When the source was raised in the dark, a blue glow

could be seen (through an appropriate mirror system) in the toluene solution, probably caused by Cerenkov radiation. It is possible that this latter violet and ultra-violet radiation was the catalyst for the side chain substitution that occurred.

The reaction mixtures from these runs were fractionally distilled under reduced pressure, since distillation at atmospheric pressure was impossible without considerable decomposition. Table II summarizes the information on one of these distillations. The overlapping temperature ranges are due to variations in pressure while changing receivers. The theoretical chlorine content for a hexachloro addition product of toluene is 69.78% Cl and it is noted that the chlorine analyses are very close to this figure.

TABLE II

HIGH BOILING FRACTIONS OBTAINED FROM REDISTILLATION
AT REDUCED PRESSURE (100-200 MICRONS Hg)
OF PRODUCTS OF REACTION BETWEEN TOLUENE AND CHLORINE

<u>Temperature</u> <u>Range °C</u>	<u>Volume</u> <u>ml.</u>	<u>%</u> <u>Cl</u>
85-102	6.6	
98-111	29.4	68.6
110-115	4.0	
111-115	18.4	69.6
112-120	18.0	70.5
120-125	3.1	
125-135	10.0	70.7

The fractions distilled over as syrupy, crystal clear liquids. After several weeks of standing, part of which was under refrigeration, some of the liquids became cloudy and crystals appeared to be precipitating out slowly. This behavior is perhaps not unusual, for if it is assumed that these materials are 1,2,3,4,5,6-hexachloro-1-methyl cyclohexane, derived from total addition of chlorine to

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toluene, at least twenty stereoisomers may be expected. It seems probable that at least half of these stereoisomers should be important constituents of the mixture of reaction products and thus it is possible that the combined effects of many mixed isomers and a high viscosity prevent appreciable crystallization of the products.

A summary of information on the runs made with toluene in the 10 kilocurie source is presented in Table III. The overall yield is based on moles of hexachloro addition products (high boiling fractions with chlorine content in the 69-71% range) obtained from a given number of moles of toluene originally placed in the apparatus. Calculation of radiation yields in micromoles per liter per kilorep and in terms of G was made, using the density which was determined from a solution of reactor contents saturated with chlorine gas.

TABLE III

SUMMARY OF THREE REACTION RUNS OF TOLUENE AND CHLORINE IN THE 10 KILO-CURIE COBALT-60 GAMMA SOURCE

Volume of Control Sample ml.	Temp., °C	Total Radiation Time min.	Esti- mated Average Gamma Flux Rate Kilorep/ hr.	Total Dose Received kilorep in air	Weight of Hexa- chloro Addi- tion Product Produced, grams	Moles Over- all Yield %	of Product Produced	Mol/ 1-kilo- rep Average	Average Value of G for Addition
1440	20	71	24	28	185	4.5	0.61	0.014	14,000
1450	20	121	22	44	371	8.8	1.2	0.017	18,000
1500	20	226	22	82	778	18	2.5	0.018	19,000

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The high values for G found in all of these cases indicates a long chain length for the reaction, about 5×10^3 or greater. This figure also assumes that each primary ionization event produces a chain of molecules which react completely and solely to give the hexachloro addition product. The fact that appreciable substitution takes place indicates that the chain length for the addition process itself might be much larger. It is very interesting that the products obtained by gamma activation differ markedly from those ordinarily obtained through actinic radiation activation of liquid toluene (mostly side chain substitution in this case). As a result of the long chains in these gamma-induced reactions, the isolated product contains negligible amounts of those molecules originally activated in the primary process. Thus, it would appear that the reaction chains in the gamma activated process were propagated by a different mechanism than those of the ultra-violet activated process.

Reaction of Toluene Derivatives

When benzylchloride, benzalchloride and benzotrichloride were each treated with chlorine in the presence of gamma radiation, there was very little reaction. The presence of benzyl chloride had a marked effect upon the reaction of benzene and chlorine, which was virtually stopped in the presence of more than one mole per cent of benzyl chloride; when less than one mole per cent of benzyl chloride was mixed with the benzene, a relatively slow reaction could be observed.

Reaction of Chlorobenzene

In another experiment, chlorobenzene was treated with chlorine gas in the 1 kilocurie cobalt-60 gamma source. In this case, the

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reaction proceeded at a rate intermediate to those of benzene and toluene. Table IV summarizes the information obtained in this run.

TABLE IV

REACTION OF CHLOROBENZENE WITH CHLORINE UNDER GAMMA-IRRADIATION

Sample Volume, ml.	Control Temp., °C	Total Reac- tion Time, min.	Gamma Flux Rate in air Kilo- rep/hr.	Total Dose Kilo- Air	Over- all Yield %	Weight of Hexa- chloro Addi- tion Pro- duct, Grams	Moles of Product Produced	Mol/l- Kilo- rep	G. for Addition
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100	20	30	52	26	12	38	0.12	0.042	43,000
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The yields are based on weight of crude product obtained by steam distilling off the unreacted chlorobenzene and drying the solid residue. For this reason yield values may be somewhat high. A sample of recrystallized material gave a chlorine analysis of 76.0, compared to the calculated value of 76.3 for the heptachloro cyclohexane which would result from addition of six chlorine atoms to chlorobenzene. The infra-red spectra of this material in carbon disulfide solution compares very closely with the spectra for heptachlorocyclohexane obtained from overchlorination of benzene as described by Daasch (4).

Chain lengths of 1.4×10^4 are indicated by the data for this reaction. Practically no reaction occurred in an experiment run under comparable conditions, but without gamma irradiation.

Experimental

Two sets of experimental equipment were used in this work. Originally, a cobalt-60 source of nominally one kilocurie

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was employed. The benzene or other aromatic compound was contained in a long glass tube placed in the center of the cobalt-60 cylinder, and chlorine was passed into the solution while a stream of cold methanol was circulated around the tube to control the temperature of the reacting mixture. A diagram of the experimental set-up is given in Fig. 1. Before each run the entire system was purged with nitrogen in order to remove all oxygen.

The second set-up was designed to allow the reaction of chlorine and larger volumes of liquid to be carried out in the radiation from a 10 kilocurie cobalt-60 source. In this equipment, up to 1.5 liters of organic liquid could be reacted with chlorine gas. The chlorine was fed from a cylinder located in the second floor chemical laboratory of the Fission Products Laboratory. Gases returning from the reacting system passed through gas wash bottles and were vented to the outdoors; this gas control system was also used in the 1 kilocurie source.

The apparatus (Fig. 2) located in the source room (Fig. 3) consisted of a water cooled reactor section, a storage section, and an inlet and exit for gases. The gases entered the apparatus through the jet injector assembly (2), then bubbled through the outer jacket of the reactor section (3), passed through bulb (5), and emerged from tube (6). In passing through the jet injector and in rising through the vertical reactor section, the gases caused the reacting liquids to circulate through the system. Vent lines at the inlet (9) and exit (10) of the apparatus were included, and were connected to dry bottles and then to mercury sealed traps so that safety was assured in case of rapid reaction or build up of gas pressure due to plugged lines.

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For the recording and controlling of temperature, thermocouples were fastened to the outside of the glass at points (11) and (12). The thermocouples were connected to chart recorders in the chemical laboratory and also activated a temperature controller, so that the temperature of the coolant circulating through the inner jacket of the reactor section (3) was controlled by the temperature of the liquid as it left the reacting section.

When ready for use, the glass reactor equipment was assembled on a support frame and placed in a portable exhaust hood adjacent to the 10 kilocurie gamma source (Fig. 3). The storage bulb section of the apparatus was usually shielded with lead bricks to prevent violent reaction of so large a quantity of material. In one run the storage bulb section (7, Fig. 2) was not shielded by lead from the direct radiation of the source, and the reaction was so violent that after only about 15 seconds of irradiation, a glass joint was blown apart as a result of the pressure of chlorine and hydrogen chloride escaping from the solution as it heated up rapidly. In another run, the shielding bricks were removed after the rate of the reaction had decreased and a marked increase in the rate resulted. In use, the reaction section could be centered as little as two inches from the gamma source. A plastic shield was placed over the open side of the hood for protection of the source room in the case of breakage of the glass reaction equipment.

After the apparatus had been set in place in the source room, it was connected to the gas control rack in the chemical laboratory by means of glass lines fitted with ball and socket ground joints. At periodic intervals the source was lowered into its well to allow

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personnel to add more dry ice to the temperature control system. When desirable, however, this part of the cooling system could also be placed out of range of the source in order to allow uninterrupted runs to be carried out.

References

1. Alyea, H. N., "Chain Reactions Produced by Light and by Alpha Radiation", J. Am. Chem. Soc., 52, 2743 (1930).
2. Weiss, J., "Chemical Dosimetry Using Ferrous and Ceric Sulfates," Nucleonics 10, 28-31 (1952). (No. 10)
3. "Isotopic Tracers and Nuclear Radiations", W. E. Siri, McGraw-Hill Book Co., Inc., New York, 1949. p. 404.
4. Daasch, L. W., "Infrared Spectroscopic Analysis of Five Isomers of 1,2,3,4,5,6-Hexachlorocyclohexane," Anal. Chem. 19, 779-85 (1947).

Figures

- I. Flow sheet for reactions of liquids with chlorine gas in the one kilo-curie cobalt-60 gamma ray source.
- II. Diagram of glass apparatus for reaction of liquids with chlorine in the 10 kilo-curie cobalt-60 gamma source.
- III. Diagram showing location of apparatus during runs in the 10 kilo-curie cobalt-60 gamma source.

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