The radiation chlorination of benzene was studied in connection with the use of nuclear radiations in the preparation of hexachlorane. The specific action of different types of radiation in the initiation of the reaction was determined by chlorinating benzene under standard conditions. The use of radiations of different energy, as can be seen from the table, led to the preparation of hexachlorocyclohexane (HCCH), differing considerably in the \( \alpha \)-isomer content.

The Effect of Various Types of Initiation on the Isomer Composition of Hexachlorocyclohexane

<table>
<thead>
<tr>
<th>Initiation</th>
<th>Concentration of chlorine, 1 g per 100 g benzene</th>
<th>( t, ^\circ C )</th>
<th>Dose rate, rad/sec</th>
<th>Dose, rad</th>
<th>Content of ( \gamma )-isomer, ( % )</th>
<th>Content of ( \alpha )-isomer, ( % )</th>
<th>Mean energy, ev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>62.1</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>No data</td>
<td>No data</td>
<td>–</td>
</tr>
<tr>
<td>Chemical (benzene peroxide)</td>
<td>14.0</td>
<td>40</td>
<td>–</td>
<td>–</td>
<td>12.7</td>
<td>63.7</td>
<td>–</td>
</tr>
<tr>
<td>Infrared radiation</td>
<td>14.0</td>
<td>40</td>
<td>–</td>
<td>–</td>
<td>12.7</td>
<td>67.0</td>
<td>0.01</td>
</tr>
<tr>
<td>Ultraviolet radiation</td>
<td>14.0</td>
<td>40</td>
<td>–</td>
<td>–</td>
<td>11.3</td>
<td>73.8</td>
<td>3 - 5</td>
</tr>
<tr>
<td>( \beta )-radiation</td>
<td>14.0</td>
<td>40</td>
<td>3.48</td>
<td>2.4 ( \times ) 10^4</td>
<td>10.2</td>
<td>78.5</td>
<td>0.4 ( \times ) 10^6</td>
</tr>
<tr>
<td>( \gamma )-radiation</td>
<td>14.0</td>
<td>40</td>
<td>6.75</td>
<td>2.4 ( \times ) 10^4</td>
<td>11.8</td>
<td>83.5</td>
<td>1.2 ( \times ) 10^6</td>
</tr>
</tbody>
</table>

With increase in the energy of radiation the content of the \( \alpha \)-isomer increased from 63.7 to 83.5\%, whereas the content of the \( \gamma \)-isomer hardly changed at all. The change in the isomer composition of the chlorination products when the reaction is initiated with high energy radiation is due to the fact that benzene takes part in the reaction not only as the reagent but also as the solvent, efficiently transmitting the absorbed energy. Under conditions of radiation chlorination of benzene energy can be transmitted from excited molecules of benzene to molecules of the dissolved substance—the intermediate products in the chlorination of benzene. Since these products can contain different amounts of the stereoisomers, the energy of formation of which differ very little [1], the additional energy action can cause isomerization of the intermediate products, which affects the isomer composition of the HCCH.

Due to the high penetrating capacity of the ionizing radiations, initiating centers are formed throughout the whole volume of the reaction mixture, whereas ultraviolet radiation is completely "extinguished" in an 18 mm
layer of the benzene solution of chlorine \( [2] \) and the chain reaction in the whole of the volume is only propagated by diffusion of the chlorine atoms. When using \( \beta \)-radiation (mean energy 0.4 Mev) the content of the \( \alpha \)-isomer depends on the thickness of the irradiated layer. Thus, in a 5 mm layer the content of the \( \alpha \)-isomer is 78.5\%, and in a 40 mm layer it falls to 61\%.

\[
\log \text{rate} = \log \text{dose rate}
\]

\[
\chi \% \alpha, \% \gamma
\]

\[
-190 -180 -170 -160 -150 -140 -130 -120 -110 -100 -90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
\]

Fig. 1. Dependence of the reaction rate on the intensity of radiation.

Fig. 3. The effect of chlorination temperature on the isomer composition of hexachlorocyclohexane.

Fig. 2. Effect of temperature on the yield of chlorination products.

In the chlorination of the \( \alpha \)-isomer of tetrachlorocyclohexene (one of the intermediate products in the chlorination of benzene) the use of a different kind of radiation (ultraviolet, infrared, \( \beta \)(Sr\(^{90}\)), \( \gamma \)(Co\(^{60}\)) resulted in a product with the same isomer composition. This is possibly due to the fact that the chlorination was carried out in a CC\(_4\) solution, which is a poor transmitter of energy.

When it is initiated by ionizing radiations, the chlorination of benzene proceeds extremely intensely, with a high energy yield. The radiation-chemical yield of the reaction reaches 853,000 per 100 ev. However, the value of \( G \) depends to a large extent on the purity of the initial products and when commercial benzene is used it drops to 130,000. The maximum radiation-chemical yield when using ultraviolet radiation (wavelength 3,650 A) is about 9,000 molecules per 100 ev.

The reaction rates in the radiation chlorination of benzene (in contrast to many photochemical chain reactions) are proportional to the square of the intensity of the radiation (Fig. 1). This dependence is observed when benzene is chlorinated without a solvent in the range of dose rates of 0.5-5 rad/sec. Dilution of the benzene with carbon tetrachloride or other solvents considerably lowers the rate of reaction.

The chlorination of benzene with initiation by ionizing radiations in the temperature range 10-40°C is a first order reaction (with regard to chlorine). The constant for the reaction rate at a dose rate of 5 rad/sec is 0.0115. With change in the dose rate the constant of the reaction rate is inversely proportional to the square of