RADIOLYSIS OF HEXACHLOROCY-CLOPENTADIENE

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Abstract

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RADIOLYSIS OF HEXACHLOROCYCLOPENTADIENE

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As we have shown earlier (1), upon γ-irradiation of two unsaturated chlorocarbons—tetrachloroethylene and hexachlorobutadiene—cleavage of a chlorine atom occurs, as does its addition to other molecules of the irradiated substance, recombination of the radicals formed upon cleavage of the chlorine atom, and subsequently again cleavage of a chlorine atom from the more complex molecules formed. The radiation-chemical yield of transformed substances at a dose of $\sim 0.5 \cdot 10^{22}$ eV/ml was 8.9 molecules/100 eV for tetrachloroethylene and 2.8 molecules/100 eV for hexachlorobutadiene. In both cases, the compounds with the highest molecular weight proved to be a mixture of isomers of composition C_8Cl_{10}.

The present work is devoted to the radiolysis of hexachlorocyclopentadiene, a compound considerably more reactive than the chlorocarbons described above, which readily enters into diene synthesis with many dienophiles, and also with itself (2). It was of interest to determine the possibility of condensation of hexachlorocyclopentadiene molecules under the action of γ-radiation through opening of double bonds or through cleavage of chlorine atoms and recombination of the radicals obtained, and to compare the radiation-chemical stability of this compound with those studied earlier (1).

Experimental Part

Technical hexachlorocyclopentadiene was distilled on a laboratory column with a Fenske packing 400 mm high. The fraction boiling within the range $89 \div 96^\circ/5.5$ mm Hg had d_4^2 1.7095; n_D^{20} 1.5651 and a freezing temperature of $8.5 \div 10^\circ$ (lit. (2, 3)).

The hexachlorocyclopentadiene isolated by rectification, in an amount of 20 ml, was loaded into ampoules made of molybdenum glass with a diameter of 20 mm, calculated so that the volume of liquid constituted two thirds of the volume of the ampoule. Since specially conducted experiments showed an insignificant

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

effect of oxygen on the processes occurring during γ-irradiation of hexachlorocyclopentadiene under conditions of applying high doses ($0.66 \cdot 10^{22} \div 15.7 \cdot 10^{22}$ eV/ml), the ampoules were sealed without prior removal of air. Irradiation was carried out at 20° on the Co^{60} installation of the Institute of Electrochemistry, Academy of Sciences of the USSR, with a dose rate from $1.95 \cdot 10^{16}$ to $3.82 \cdot 10^{16}$ eV/ml · sec, determined by the ferrous-sulfate method. After irradiation the ampoules were opened, the constants of the reaction liquid were determined, the unreacted substance was distilled off, and the residue was separated by rectification in vacuum, followed by freezing out of the crystals formed in individual fractions after prolonged (10-15 days) standing. The isolated substances were identified analogously to (1), also using for determination of molecular weight the method of isothermal distillation (4) from chloroform with hexachloro-4-dichloromethylcyclopentene as a standard.

Results of the Experiments and Their Discussion

In the course of γ-irradiation the contents of the ampoules changed color from yellowish to dark brown; the constants of the irradiated substance increased (Fig. 1). At a dose of $15.7 \cdot 10^{22}$ eV/ml, the irradiation products were a very viscous, resin-like dark-brown mass. In all experiments the absence of molecular chlorine was established. With increasing dose the degree of conversion at first increases rapidly, then more slowly, while the radiation-chemical yield decreases (Fig. 2).

At 50% conversion the total radiation-chemical yield of converted substances is $\sim$ 5 molecules/100 eV. Among the products formed upon γ-irradiation of hexachlorocyclopentadiene, a white crystalline substance was isolated which, after twofold recrystallization from benzene, melted at $41.3 \div 41.5$°. Its amount in different experiments was $20 \div 30$% of the reacted hexachlorocyclopentadiene. The isolated substance was identified by us as octachlorocyclopentene.

Fig. 1. Dependence of the constants of the reaction liquid on the irradiation dose.
1 —relative change in specific gravity; 2 —relative change in refractive index; 3 —relative viscosity (relative to the initial substance)

Fig. 2. Effect of dose on the degree of conversion of cyclo-C_5Cl_6 (1) and on the radiation-chemical yield of irradiation products (2)

Found, %: C 17.26; Cl 82.28

Fig. 3. IR spectra of bis-(pentachlorocyclopentadienyl) (I) and of crystals with m.p. 110.1-110.3°, isolated from the irradiation products of cyclo-C_5Cl_6 (II)

Figure 3: Fig. 3. IR spectra of bis-(pentachlorocyclopentadienyl) (I) and of crystals with m.p. 110.1-110.3°, isolated from the irradiation products of cyclo-C_5Cl_6 (II)

cyclo-C_5Cl_8. Calculated, %: C 17.41; Cl 82.59

The molecular weight was found by isothermal distillation. Found: 347; calculated: 344.

The structure of the substance was confirmed by IR spectral data.

From the reaction mass there was also isolated a viscous red oil in an amount of $\sim 50\%$ of the weight of the reacted substance, boiling in the range $180 \div 188^{\circ}/3$ mm Hg (n_D^{50} 1.6049; d_4^{50} 1.8085), corresponding to the composition $C_{10}Cl_{10}$.

Found, %: Cl 74.14
$C_{10}Cl_{10}$. Calculated, %: Cl 74.73

The molecular weight was found by isothermal distillation. Found: 483; calculated: 475.

In a small amount ($1 \div 2\%$ of the weight of the reacted hexachlorocyclopentadiene), crystals were isolated which, after threefold recrystallization from benzene and then from a methanol-carbon tetrachloride mixture, had a yellowish tint and melted at 110.1—110.3°.

The molecular weight of these crystals and their chlorine content proved to be very close to those for bis-(pentachlorocyclopentadienyl).

Found, %: Cl 75.01
$C_{10}Cl_{10}$. Calculated, %: Cl 74.74

Molecular weight found: cryoscopic, 458; isothermal distillation, 485; calculated, 475.

However, the melting point of this compound did not correspond to that for bis-(pentachlorocyclopentadienyl) (5).

In the ultraviolet spectrum of the compound isolated by us, a band is observed with λ_{max}273 mμ, ε_{max}5000, and a less intense band with λ_{max}320 mμ, ε_{max}3200, whereas in the ultraviolet spectrum of the bis-(pentachlorocyclopentadienyl) synthesized by us, for λ_{max}280 mμ, ε_{max}2000, and for λ_{max}330 mμ, ε_{max}2700.

The difference in the structure of the two compounds is also confirmed by their IR spectra (Fig. 3).

Fig. 3. IR spectra of bis-(pentachlorocyclopentadienyl) *(I)* and of crystals with m.p. 110.1-110.3°, isolated from the irradiation products of cyclo-C_5Cl_6 *(II)*.

At the boiling temperature $\sim 190^\circ/4$ mm Hg, a very small amount of crystals was also isolated, melting at 340—342°; the melting point of these crystals and their elemental composition proved to be very close to those for tetracyclic chlorocarbon $C_{15}Cl_{12}$, m.p. 345—347°, isolated by Mark (6) from the products of dechlorination of hexachlorocyclopentadiene under the action of ethyl phosphite.

Found, %:	C 29.93; Cl 69.75
$C_{15}Cl_{12}$. Calculated, %:	C 29.70; Cl 70.30

In the ultraviolet spectrum of this compound, two bands are observed: λ_{max}268 and 278 mμ, which is in good agreement with the data of Mack Bi (7) for this compound.

On the basis of the set of identified compounds, we give the most probable scheme of transformations of hexachlorocyclopentadiene in the course of its γ-irradiation:

$$\text{cyclo-}C_5Cl_6 \xrightarrow{\gamma} \begin{cases} C_5Cl_5^\bullet\ (I) + Cl^\bullet, \\ C_5Cl_5^\bullet\ (II) + Cl^\bullet, \\ C_5Cl_5^\bullet\ (III) + Cl^\bullet, \end{cases}$$

$$Cl^\bullet + \text{cyclo-}C_5Cl_6 \longrightarrow C_5Cl_7^\bullet \xrightarrow{\text{cyclo-}C_5Cl_6} C_{10}Cl_{12} + R^\bullet,$$

where $R^\bullet$ may be I, II, or III.

The recombination of the radicals formed, I, II, and III, can lead to the formation of six structures:

I–I	I–III	II–III
[[chemical structural formula]]	[[chemical structural formula]]	[[chemical structural formula]]
I–II	**II–II**	**III–III**
[[chemical structural formula]]	[[chemical structural formula]]	[[chemical structural formula]]

However, radicals I, II, and III are not equivalent, since only in the first does the unpaired electron participate in conjugation with two π-bonds. This radical is apparently capable of adding to the double bond of hexachlorocyclopentadiene, forming structures I–II and I–III according to the scheme:

[[radical I structural formula]]+[[hexachlorocyclopentadiene structural formula]] $\longrightarrow$ { [[intermediate structura
[[intermediate structura

As a consequence of the above, for the substance with m.p. 110.1—110.3°, precisely these two structures are the most probable, which is partly confirmed by spectroscopic data. In the ultraviolet spectrum of compounds described by structural formulas II–II, II–III, and III–III, intense absorption bands with λ_{max}260—280 mμ and ε_{max}20 000—50 000 would be expected ([8]).

Thus, in the γ-radiolysis of hexachlorocyclopentadiene, processes occur that are analogous to those described for tetrachloroethylene and hexachlorobutadiene. In the present case there also take place cleavage of a chlorine atom, its addition to other molecules of the irradiated substance, recombination of the radicals obtained and their interaction with the starting substance, and subsequently again cleavage of a chlorine atom from the compounds formed.

At the same time, the products formed during the autocondensation of hexachlorocyclopentadiene and in its diene synthesis were not detected by us.

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