Chemistry

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Fig. 1

Figure 1: Fig. 1

Abstract

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RADIOLYSIS OF TETRACHLOROETHYLENE AND HEXACHLOROBUTADIENE

Along with the comparatively large amount of information on the radiolysis of unsaturated hydrocarbons, there is very little information on the transformations of chlorine-containing olefins and diolefins under the action of γ-radiation. It is known, however, that the radiation-chemical stability of chlorinated ethylenes increases with an increase in the number of chlorine atoms in the molecule [(1)]. In this connection, the behavior of completely chlorinated unsaturated hydrocarbons during irradiation is of great interest, since many of these compounds are inert under the usual methods of action on molecules. Thus, tetrachloroethylene and hexachlorobutadiene do not change at 500° [(2)], hexachlorobutadiene does not polymerize at 100 atm [(3)], and tetrachloroethylene withstands a pressure of 2000 atm at 200° [(4)].

There is only one study [(1)] in which, along with partially chlorinated ethylenes, γ-irradiation of the simplest representative in the series of unsaturated chlorohydrocarbons—tetrachloroethylene—is considered at comparatively low doses.

Fig. 1. Dependence of the constants of the reaction product on the γ-irradiation dose. $1, 1'$—relative changes in specific gravities, $2, 2'$—relative changes in refractive indices, $3, 3'$—relative viscosities ($1, 2, 3$—for C_2Cl_4, $1', 2', 3'$—for C_4Cl_6).

The present investigation is devoted to the γ-irradiation of tetrachloroethylene and hexachlorobutadiene and is the beginning of a study of the influence of the structure of lower unsaturated chlorohydrocarbons on the processes occurring during the radiolysis of these compounds.

Experimental Part

The starting substances were dried over calcium chloride and distilled with a reflux condenser. The distilled compounds had physical constants close to the literature data. Samples with a volume of 20 mm were loaded into molybdenum-glass ampoules 20 ml in diameter, calculated so that the volume of liquid was

Fig. 2

Figure 2: Fig. 2

two thirds of the ampoule volume. The ampoules were sealed without removal of air, since preliminary experiments showed that the amount of substances formed does not depend on the presence of oxygen under γ-irradiation conditions with significant doses.

γ-Irradiation was carried out on a Co^{60} installation of the Institute of Electrochemistry of the Academy of Sciences of the USSR at a dose rate of $3.19 \cdot 10^{16}$ eV/ml·sec for tetrachloroethylene and $3.30 \cdot 10^{16}$ eV/ml·sec for hexachlorobutadiene, determined by the ferrosulfate method. The dose was varied from $0.5 \cdot 10^{22}$ to $1.4 \cdot 10^{23}$ eV/ml.

After irradiation, the ampoules were opened and the content of molecular chlorine (iodometrically), the specific gravity, the refractive index, and the relative viscosity of the reaction product were determined. The unreacted substance was distilled off and the residue was subjected to rectification. The isolated compounds were identified by boiling or melting points, specific gravities, refractive indices, molecular weights, elemental analysis, and IR spectra.

Results of the experiments and their discussion

(Figs. 1, 2; Table 1)

Among the products formed upon irradiation of tetrachloroethylene with γ-rays, the following were isolated and identified: hexachloroethane (m.p. 180.5-181.5°, mol. wt. 227; C 10.0%), hexachlorobutadiene (b.p. 60-61°/3.5 mm, n_D^{20} 1.5550), a fraction with b.p. 120-130°/3.5 mm and n_D^{20} 1.5800, apparently containing octachlorobutene (literature data: b.p. 97-97.5°/0.1 mm, n_D^{20} 1.5787), hexachloro-4-dichloromethylenecyclopentene (m.p. 180-182°, mol. wt. 338; C 20.62%, Cl 79.73%), a red viscous oil with b.p. 180-210°/3.5 mm, and traces of chlorine.

Fig. 2. Effect of irradiation dose on the degrees of conversion $(1, 1')$ and radiation-chemical yields $(2, 2')$
$(1, 2$ –for C_2Cl_4, $1', 2'$ –for $C_4Cl_6)$

The set of products is consistent with (1), despite the use of a considerably (almost 70-fold) larger dose. The use of the indicated doses made it possible to obtain high degrees of conversion and to study in greater detail the nature of the red oil. On the basis of elemental analysis—Cl 77.9%, molecular weight 443, and molar refraction 80.7—it was found that the isolated red oil corresponds to the composition C_8Cl_{10} (Cl 78.6%, mol. wt. 451) and apparently represents a mixture of isomers of linear structure (MR81.5).

The main products formed upon irradiation of hexachlorobutadiene proved to

be: hexachloroethane (m.p. 181–182°; mol. wt. 229; C 9.95%), a red viscous oil with b.p. 185–220°/4 mm, and a nondistillable dark-brown resin-like residue. Chlorine was not detected.

The molecular weight of the red oil was 448; its elemental composition—Cl 77.6% —and IR spectrum (Fig. 3) proved to be very close to those for the red oil isolated from the products formed upon irradiation of tetrachloroethylene with γ-rays. This fact indicates that the red oil of composition C_8Cl_{10}, obtained in the γ-irradiation of tetrachloroethylene, is formed from the intermediate product—hexachlorobutadiene.

As can be seen from Fig. 2, the total radiation-chemical yields in the γ-irradiation of both compounds decrease with increasing irradiation dose; moreover, the yields of the irradiation products of tetrachloroethylene are 3–5 times higher than the yields of products formed in the γ-irradiation of hexachlorobutadiene. Thus, $G_{\max}$ for C_2Cl_4 at a dose of $0.5 \cdot 10^{22}$ eV/ml reaches

Table 1

Effect of dose and irradiated substances on the composition of the products formed (in wt. percent)

Dose, eV/ml · 10^-22	C_2Cl_6	C_4Cl_6	C_4Cl_8*	C_6Cl_8	C_8Cl_{10}	cubic residue Cl >75%	Sum of C_8Cl_{10} and cubic residue
γ-irradiation of tetrachloroethylene							
0.54	35	30	12	3	25	5	30
1.24	37	28	2	not determined	26	7	33
2.88	42	24	10	1	19	4	23
5.76	53	18	8	5	10	16	26
8.18	66	11	7	2	—	—	14

Fig. 3. IR transmission spectra of oils of composition C_8Cl_{10}, isolated from products formed upon γ-irradiation of C_2Cl_4 (I) and C_4Cl_6 (II)

Figure 3: Fig. 3. IR transmission spectra of oils of composition C_8Cl_{10}, isolated from products formed upon γ-irradiation of C_2Cl_4 (I) and C_4Cl_6 (II)

Dose, eV/ml · 10^-22	C_2Cl_6	C_4Cl_6	C_4Cl_8*	C_6Cl_8	C_8Cl_{10}	cubic residue Cl >75%	Sum of C_8Cl_{10} and cubic residue
γ-irradiation of hexachlorobutadiene							
1.49	2	–	0	0	91	7	98
2.78	8	–	0	0	–	–	92
2.99	12	–	0	0	–	–	88
6.01	22	–	0	0	62	16	78
8.49	24	–	0	0	48	28	76
13.60	28	–	0	0	–	–	72

* Intermediate fraction, conventionally taken as octachlorobutene.

8.8 molecules/100 eV, whereas G_{max} for C_4Cl_6 at this same dose is only 2.8 molecules/100 eV.

When considering the effect of the irradiated compound and the dose on the composition of the chlorohydrocarbons formed (see Table 1), it should be borne in mind that the most accurate results were obtained for hexachloroethane and for the red oil of composition C_8Cl_{10}. For the remaining products only the order of magnitude is valid.

Fig. 3. IR transmission spectra of oils of composition C_8Cl_{10}, isolated from products formed upon γ-irradiation of C_2Cl_4 (I) and C_4Cl_6 (II)

An increase in the content of hexachloroethane with increasing dose in the products formed during γ-irradiation of both tetrachloroethylene and hexachlorobu-

–diene, indicates the radiation-chemical stability of this compound.

The formation of hexachloroethane occurs simultaneously with the formation of more complex molecules containing a smaller amount of chlorine than the irradiated compounds.

The presence of hexachlorobutadiene among the products formed during the γ-irradiation of tetrachloroethylene, even in the case of the highest doses, confirms our conclusion that it has greater radiation-chemical stability than tetrachloroethylene (Figs. 1 and 2).

Thus, in the radiolysis of tetrachloroethylene and hexachlorobutadiene at the irradiation doses used by us, complex processes occur involving chlorine migration and condensation of the reacting molecules, and, in the case of hexachlorobutadiene, their partial destruction.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.